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MATHEMATICS

On Linear Functional Equations in Hilbert Space

by

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1. Note [1] gives a fixed point theorem for a weakly continuous operator in Hilbert space. The main results obtained in the present note are a consequence of this theorem. Since every bounded linear operator is weakly continuous, it is natural to apply these results to the theory of linear equations in Hilbert space. The questions studied here are linked to the inversion problem of some bounded linear operators working in separable real Hilbert spaces. Non-local theorems concerning the parameter are here stated. An estimate for the norm of the inverse operator is also given. Moreover, it is stated that the Galerkin method is applicable to the class of linear equations examined. It should be emphasised that Galerkin's approaches to the solution exist for every index in the case considered, while in the general case, under the additional condition that the operator in question is completely continuous, the existence of such approaches is stated only for sufficiently large indices. But without the additional assumption of complete continuity of the operator, it can only be asserted that in this case Galerkin's process converges weakly to a solution of the equation. This note also contains some applications of the results obtained to the theory of infinite systems of ordinary linear equations and to the theory of integral equations. In some special cases an estimate is also given of the Galerkin's method.

2. Let H be a real separable Hilbert space. Denote by Q the sphere in H with centre in 0 of radius r, where 0 is the zero-element of the space, i. e., Q is the set of all elements x of H satisfying the inequality $\|x\| \leqslant r$. The boundary of Q, i. e., the set of all elements of H satisfying the equation $\|x\| = r$, is denoted by S. Let F be a weakly continuous (generally non-linear) operator defined on Q with values in H.

Consider the non-linear equation

$$x - Fx = y, \tag{1}$$

THEOREM 1. *Let us assume that there exists a positive number* $M<1$ *such that*

$$(Fx,x)\leqslant M(x,x) \quad \text{for every} \quad x \text{ of } S. \tag{2}$$

Then for every y *of the sphere with centre in* 0 *of radius* $(1-M)r$, *i.e, for* $\|y\|\leqslant(1-M)r$, *there exists in* Q *at least one solution of Equation* (1).

Theorem 1 follows from Theorem 2 of [1].

Let (e_n), $(n=1,2,...)$ be an orthonormal complete system in a separable Hilbert space. Denote by H_n the n-dimensional space spanned by the elements e_i $(i=1,2,...,n)$. If x_n is of the form

$$x_n=\sum_{i=1}^{n} c_i^{(n)} e_i,$$

where the numbers $c_i^{(n)}$ are defined by the system of equations

$$c_i^{(n)}-(Fx_n,e_i)=(y,e_i) \quad (i=1,2,...,n), \tag{4}$$

then x_n is a Galerkin approach to the solution of Equation (1).

THEOREM 2. *If the assumptions of Theorem* 1 *are fulfilled, then for every* n $(n=1,2,...)$ *there exists a Galerkin approach* $x_n\in H_n\cdot Q$. *If* (x_n), *where* $x_n\in H_n\cdot Q$, *is a sequence of Galerkin approaches, then there exists a sub-sequence* (x_{n_i}), *which converges weakly to a solution of Equation* (1). *Every weakly convergent sub-sequence* (x_{n_p}), $x_{n_p}\in H_{n_p}\cdot Q$ *of Galerkin approaches converges weakly to a solution of Equation* (1). *If Equation* (1) *has only one solution in* Q, *then the sequence* (x_n) *of Galerkin approaches converges weakly to this solution.*

Remark 1. The condition of weak continuity in Theorems 1 and 2 can be replaced by that of complete continuity; then the weak convergence in Theorem 2 could be replaced everywhere by strong convergence.

3. Let A be a bounded linear operator defined on H with values in H. Let us assume that there exists a positive number $M<1$ such that

$$(Ax,x)\leqslant M(x,x) \quad \text{for every} \quad x \text{ of } H. \tag{5}$$

Consider the linear equation

$$x-Ax=y. \tag{6}$$

Applying Theorem 1 we obtain

THEOREM 3. *If condition* (5) *is satisfied, then Equation* (6) *has for any* y *of* H *only one solution. The inverse operator* $(I-A)^{-1}$ *is bounded, and its norm* $\|(I-A)^{-1}\|\leqslant\|(1-M)^{-1}\|$ *).

*) I denotes the identity.

Remark 2. Theorem 3 may be regarded as a generalisation (in a real separable Hilbert space) of the well-known theorem on the existence of the operator $(I-A)^{-1}$ when $\|A\|<1$.

Now consider the linear equation with a parameter,

$$x-Ax=y. \tag{7}$$

By Theorem 3 we have

THEOREM 4. *Let us assume that one of the following conditions is satisfied:*

$$\lambda K<1 \quad \text{and} \quad \lambda>0, \quad \text{where} \quad K=\sup_{\|x\|=1}(Ax,x), \tag{8}$$

$$\lambda k<1 \quad \text{and} \quad \lambda<0, \quad \text{where} \quad k=\inf_{\|x\|=1}(Ax,x). \tag{9}$$

Then Equation (7) *has only one solution for any* y *of* H. *The inverse operator* $(I-A)^{-1}$ *is bounded and its norm*

$$\|(I-A)^{-1}\|\leqslant(1-\lambda K)^{-1} \quad \textit{under condition (8)},$$

or

$$\|(I-A)^{-1}\|\leqslant(1-\lambda k)^{-1} \quad \textit{under condition (9)}.$$

As a consequence of Theorem 2 we obtain

THEOREM 5. *Suppose that the conditions of Theorem* 3 *or* 4 *are fulfilled. Then for every* n *there exists exactly one Galerkin approach to the solution and the sequence of these approaches converges weakly to the solution of Equation* (7), *whose existence is assured by Theorem* 3 *or* 4. *Under the additional condition that the operator* A *is completely continuous the convergence is strong.*

4. We shall now give an application of the above theorem to the theory of linear integral equations.

Let G be a closed bounded subset of a finite dimensional Euclidean space. Denote by $L_2(G)$ the real Hilbert space of all square integrable functions on G. Consider the linear integral equations

$$x(s)-\int_G A(s,t)x(t)\,dt=y(s), \tag{10}$$

$$x(s)-\lambda\int_G A(s,t)x(t)\,dt=y(s), \tag{11}$$

where $s,t\in G$ and $x,y\in L_2(G)$.

Suppose that the kernel $A(s,t)$ defines a bounded linear operator with domain and range in $L_2(G)$. Condition (5) here means

$$\int_G\int_G A(s,t)x(t)x(s)\,dt\,ds\leqslant M\int_G x^2(t)\,dt, \qquad 0<M<1. \tag{12}$$

Replacing the scalar product in (8) and (9) by the corresponding expression we can formulate Theorems 3—5 for Equations (10) and (11).

Assuming that the kernel $A(s,t)$ satisfies the condition

$$\int_G \int_G A^2(s,t)\,ds\,dt < \infty, \tag{13}$$

then it is known that the linear operator A defined by the kernel $A(s,t)$ is completely continuous in $L_2(G)$. Hence the Galerkin approaches x_n whose existence and uniqueness are assured by (12) for every n, converge strongly to the unique solution of Equation (10). Moreover, we have the following estimate for the convergence of Galerkin's process.

If conditions (12) and (13) are satisfied, then

$$\|x_n \quad x\| \leqslant \frac{1}{1-M}\left[\left(\|y\|^2 - \sum_{i=1}^{n} |(y,e_i)|^2\right)^{1/2} + \frac{\|y\| C_n}{1-M-C_n}\right]$$

for n such that $C < 1-M$, where

$$C_n^2 = \int_G \int_G A^2(s,t)\,ds\,dt - \sum_{i=1}^{n} \int_G \left[\int_G A(s,t)\,e_i(s)\,ds\right]^2 dt,$$

(e_i) is a complete orthonormal system in $L_2(G)$, x_n denotes the Galerkin approach to the solution x of Equation (10).

A similar estimate can also be obtained for Equation (11).

5. In the same way we can obtain an application to the theory of infinite systems of ordinary linear equations.

Consider the infinite systems of real linear equations of the form

$$x_i - \sum_{k=1}^{\infty} a_{ik} x_k = y_i \qquad (i = 1,2,\ldots), \tag{14}$$

$$x_i - \lambda \sum_{k=1}^{\infty} a_{ik} x_k = y_i \qquad (i = 1,2,\ldots), \tag{15}$$

where the matrix (a_{ik}) defines a bounded linear operator with domain and range in the real space l_2 of all square summable sequences $x = (x_i)$, where $\sum_{i=1}^{\infty} x_i^2 < \infty$. Condition (5) here means

$$\sum_{i=1}^{\infty} \sum_{k=1}^{\infty} a_{ik} x_k x_i \leqslant M \sum_{i=1}^{\infty} x_i^2, \qquad 0 < M < 1. \tag{16}$$

It is easy to formulate Theorems 3—5 for Equations (14) and (15).

Now let us assume that the matrix (a_{ik}) satisfies the following condition:

$$\sum_{i=1}^{\infty}\sum_{k=1}^{\infty} a_{ik}^2 < \infty. \tag{17}$$

Condition (17) implies that the operator A defined by the matrix (a_{ik}) is completely continuous in l_2.

As a complete orthonormal system in l_2 we take the sequence $e_1 = (1,0,\ldots)$, $e_2 = (0,1,\ldots)$, ... Then Galerkin's approaches are of the form $x^{(n)} = \sum_{i=1}^{n} c_i^{(n)} e_i$, where the numbers $c_i^{(n)}$ are solutions of the system of equations

$$c_i^{(n)} - \sum_{k=1}^{n} a_{ik} c_k^{(n)} = y_i \qquad (i = 1,2,\ldots,n).$$

As in **4.** we can assert that Galerkin's approaches $x^{(n)}$, whose existence is assured by (16) converge strongly to the unique solution of Equation (15). If (17) and (16) are satisfied, then

$$\|x^{(n)} - x\| \leqslant \frac{1}{1-M}\left[\left(\sum_{i=n+1}^{\infty} y_i^2\right)^{1/2} + \frac{\|y\| C_n}{1-M-C_n}\right], \tag{ii}$$

for n such that $C_n < 1-M$, where

$$C_n^2 = \sum_{i=1}^{\infty}\sum_{k=1}^{\infty} a_{ik}^2 - \sum_{i=1}^{\infty}\sum_{k=1}^{n} a_{ik}^2,$$

(i) and (ii) result from the following general estimate:

$$\|(I-A_n)^{-1} f_n - (I-A)^{-1}\| \leqslant \|(I-A)^{-1}\| \, \|f_n - f\| + \frac{\|(I-A)^{-1}\|^2 \, \|A_n - A\| \cdot \|f\|}{1 - \|(I-A)^{-1}\| \cdot \|A_n - A\|}$$

for sufficiently large n, where $\|A_n - A\| \to 0$ as $n \to \infty$.

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MATHEMATICS

On the Method of Orthogonal Projection

by

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1. In the present paper we are concerned with the estimate of error for the method of orthogonal projection. At the same time we give an economical and compact reckoning scheme. This scheme is based upon the method of papers [1], and [2]. Although in order to estimate the error we must apply two different processes, yet, using the above mentioned computation scheme, we obtain an economy computation as follows. We need not find all approximate solutions in consecutive order until we get a suitable one. But we find the error estimates for the corresponding approximate solutions in consecutive order by a recurrent formula until we get a suitable one and only then do we find the corresponding approximate solution. In order to apply the method of orthogonal projection we must construct a corresponding Hilbert space for the given problem. The solution of the problem consists in splitting this auxiliary Hilbert space into two orthogonal subspaces such that the orthogonal projection of a given function onto one of the subspaces gives the required solution. From this point of view the following statement of the problem in a general form is expedient.

Let $\mathfrak{H}$ be a Hilbert space and let $\mathfrak{P} \subset \mathfrak{H}$ be a linear subspace of $\mathfrak{H}$. Denote by $\mathfrak{Q}$ the orthogonal complement of $\mathfrak{P}$ in $\mathfrak{H}$. Then $\mathfrak{H}$ is a direct sum of $\mathfrak{P}$ and $\mathfrak{Q}$: $\mathfrak{H} = \mathfrak{P} \oplus \mathfrak{Q}$.

Given a linearly independent system $(e_i) \subset \mathfrak{P}$, $i = 1, 2, \ldots$ complete in $\mathfrak{P}$ and a linearly independent system $e_i' \subset \mathfrak{Q}$, $i = 1, 2, \ldots$ complete in $\mathfrak{Q}$.

2. Let f be a given element of $\mathfrak{H}$ such that f non $\epsilon \mathfrak{P}$ and f non $\epsilon \mathfrak{Q}$.

The problem consists in finding the approximate orthogonal projection x_n of f into $\mathfrak{P}$ such that $\|x_n - x\| < \varepsilon$, where $x = Pf$ is the orthogonal projection of f into $\mathfrak{P}$ and ε is an arbitrary fixed positive number.

In order to find the solution of the stated problem we denote by $\mathfrak{P}_k$ the linear space spanned by the elements $e_1, e_2, \ldots, e_k$ and by P_k — the orthogonal projection of $\mathfrak{H}$ onto $\mathfrak{P}_k$.

Putting $x_k=P_kf$ for $k=1,2,...$, we obtain

$$(1) \qquad x_k\to x=Pf, \quad \text{as} \quad k\to\infty \qquad \|x_k\|<\|x_{k+1}\|\leqslant\ldots\leqslant\|x\|.$$

Denote by $\mathfrak{Q}_k$ the linear space spanned by the elements $e'_1,e'_2,...,e'_k$, by Q_k the orthogonal projection of $\mathfrak{H}$ onto $\mathfrak{Q}_k$, and by Q the orthogonal projection of $\mathfrak{H}$ onto $\mathfrak{Q}$. Setting

$$x'_k=f-Q_kf,$$

we obtain

$$(2) \qquad x'_k\to f-Qf=x, \quad \text{as} \quad k\to\infty \quad \text{and} \quad \|x\|\leqslant\ldots\leqslant\|x'_{k+1}\|\leqslant\|x'_k\|.$$

Since $0<\|x'_k\|-\|x_k\|\to 0$ as $k\to\infty$ we can choose an index n such that $\|x'_n\|^2-\|x_n\|^2<\varepsilon^2$.

Then, by (1), (2) we obtain

$$(3) \qquad \|x_n-x\|^2=\|x\|^2-\|x_n\|^2\leqslant\|x'_n\|^2-\|x_n\|^2<\varepsilon^2.$$

3. Now we give a computation scheme based upon the method of [1].

In order to find the orthogonal projections P_k and Q_k we transform the systems e_k and e'_k into orthogonal systems e_k and e'_k, respectively:

$$(4) \qquad \begin{aligned} &e_1=\bar{e}_1 && e'_1=\bar{e}'_1\\ &e_2=\gamma_{21}\bar{e}_1+\bar{e}_2 && e'_2=\gamma_{21}\bar{e}'_1+\bar{e}'_2\\ &e_3=\gamma_{31}\bar{e}_1+\gamma_{32}\bar{e}_2+\bar{e}_3 && e'_3=\gamma'_{31}\bar{e}'_1+\gamma'_{32}\bar{e}'_2+\bar{e}'_3\\ &\ldots\ldots\ldots\ldots && \ldots\ldots\ldots\ldots, \end{aligned}$$

where the triangle matrices (γ_{ki}) and (γ'_{ki}) are obtained from the corresponding Gram matrices of elements $\alpha_{ki}=(e_k,e_i)$ and $\alpha'_{ki}=(e'_k,e'_i)$ respectively, using the method of [1]. On the basis of (4) we compute the coefficients $b_k=(\overline{f,\bar{e}_k})$ and $b'_k=(\overline{f,\bar{e}'_k})$ as follows:

$$(5) \qquad \begin{aligned} &b_1=(e_1,f), && b'_1=(e'_1,f),\\ &b_k=(e_k,f)-\sum_{i=1}^{k-1}\gamma_{ki}b_i, && b'_k=(e'_k,f)-\sum_{i=1}^{k-1}\gamma'_{ki}b'_i. \end{aligned}$$

By [1] we have

$$(6) \qquad \delta_k=\|x_k\|^2=\sum_{i=1}^{k}\frac{|b_i|^2}{\beta_{ii}}=\delta_{k-1}+\frac{|b_k|^2}{\beta_{kk}} \quad \text{and} \quad \delta_1=\frac{|b_1|^2}{\beta_{11}}.$$

Since

$$\|x'_k\|^2=\|f-Q_kf\|^2=\|f-Qf\|^2+\|Qf-Q_kf\|^2=\|f\|^2-\|Qf\|^2+\|Qf\|^2-\|Q_kf\|^2,$$

we obtain

$$(7) \qquad \delta'_k=\|x'_k\|^2=\|f\|^2-\|Q_kf\|^2=\delta'_{k-1}-\frac{|b'_k|^2}{\beta'_{kk}} \quad \text{and} \quad \delta'_1=\|f\|^2-\frac{|b'_1|^2}{\beta'_{11}}.$$

4 $\overset{0}{\delta}_1=\overset{2}{\delta}_1-\overset{1}{\delta}_1$	3 $\check{\delta}_1=\frac{1}{\check{\beta}_{11}}\lvert b_1\rvert^2$	2 $\check{b}_1=\check{l}_1$	1 $\check{\beta}_{11}=\check{\alpha}_{11}$	
9 $\overset{0}{\delta}_2=\overset{2}{\delta}_2-\overset{1}{\delta}_2$	8 $\check{\delta}_2=\check{\delta}_1+\frac{1}{\check{\beta}_{22}}\lvert\check{b}_2\rvert^2$	7 $\check{b}_2=\check{l}_2-\check{\gamma}_{21}\check{b}_1$	5 $\check{\beta}_{21}=\check{\alpha}_{21}$ $\check{\gamma}_{21}=\frac{1}{\check{\beta}_{11}}\check{\beta}_{21}$	6 $\check{\beta}_{22}=\check{\alpha}_{22}-\bar{\check{\gamma}}_{21}\check{\beta}_{21}$
15 $\overset{0}{\delta}_3=\overset{2}{\delta}_3-\overset{1}{\delta}_3$	14 $\check{\delta}_3=\check{\delta}_2+\frac{1}{\check{\beta}_{33}}\lvert\check{b}_3\rvert^2$	13 $\check{b}_3=\check{l}_3-\sum_{i=1}^{2}\check{\gamma}_{3i}\check{b}_i$	10 $\check{\beta}_{31}=\check{\alpha}_{31}$ $\check{\gamma}_{31}=\frac{1}{\check{\beta}_{11}}\check{\beta}_{31}$	11 $\check{\beta}_{32}=\check{\alpha}_{32}-\bar{\check{\gamma}}_{21}\beta_{31}$ $\check{\gamma}_{32}=\frac{1}{\check{\beta}_{22}}\check{\beta}_{32}$
22 $\overset{0}{\delta}_4=\overset{2}{\delta}_4-\overset{1}{\delta}_4$	21 $\check{\delta}_4=\check{\delta}_3+\frac{1}{\check{\beta}_{44}}\lvert\check{b}_4\rvert^2$	20 $\check{b}_4=\check{l}_4-\sum_{i=1}^{3}\check{\gamma}_{4i}\check{b}_i$	16 $\check{\beta}_{41}=\check{\alpha}_{41}$ $\check{\gamma}_{41}=\frac{1}{\check{\beta}_{11}}\check{\beta}_{41}$	17 $\check{\beta}_{42}=\check{\alpha}_{42}-\bar{\check{\gamma}}_{21}\beta_{41}$ $\check{\gamma}_{42}=\frac{1}{\check{\beta}_{22}}\check{\beta}_{42}$
. . . .	. . . . .	. . . . .	. . . . .	. . . . .
$\overset{0}{\delta}_k=\overset{2}{\delta}_k-\overset{1}{\delta}_k$	$\check{\delta}_k=\check{\delta}_{k-1}+\frac{1}{\check{\beta}_{kk}}\lvert\check{b}_k\rvert^2$	$\check{b}_k=\check{l}_k-\sum_{i=1}^{k-1}\check{\gamma}_{ki}\check{b}_i$	$\check{\beta}_{k1}=\check{\alpha}_{k1}$ $\check{\gamma}_{k1}=\frac{1}{\check{\beta}_{11}}\check{\beta}_{k1}$	$\check{\beta}_{k2}=\check{\alpha}_{k2}-\bar{\check{\gamma}}_{21}\check{\beta}_{k1}$ $\check{\gamma}_{k2}=\frac{1}{\check{\beta}_{22}}\check{\beta}_{k2}$
. . . .	. . . . .	. . . . .	. . . . .	. . . . .
$\overset{0}{\delta}_n=\overset{2}{\delta}_n-\overset{1}{\delta}_n$	$\check{\delta}_n=\check{\delta}_{n-1}+\frac{1}{\check{\beta}_{nn}}\lvert\check{b}_n\rvert^2$	$\check{b}_n=\check{l}_n-\sum_{i=1}^{n-1}\check{\gamma}_{ni}\check{b}_i$	$\check{\beta}_{n1}=\check{\alpha}_{n1}$ $\check{\gamma}_{1n}=\frac{1}{\check{\beta}_{11}}\check{\beta}_{n1}$	$\check{\beta}_{n2}=\check{\alpha}_{n2}-\bar{\check{\gamma}}_{21}\check{\beta}_{n1}$ $\check{\gamma}_{n2}=\frac{1}{\check{\beta}_{22}}\check{\beta}_{n2}$

Notations: $\nu=1,2$ $\quad \overset{1}{a}_{ki}=a_{ki}=(e_k,e_i)$ $\quad \overset{1}{l}_i=(e_k,f);\ \overset{1}{b}_i=b_i$ $\quad \overset{1}{\gamma}_{ik}=\gamma_{ik}$ $\quad \overset{1}{\beta}_{ik}=\beta_{ik}$

$\overset{2}{a}_{ki}=a'_{ki}=(e'_k,e'_i)$ $\quad \overset{2}{l}_i=(e'_k,f);\ \overset{2}{b}_i=b'_i$ $\quad \overset{2}{\gamma}_{ik}=\gamma'_{ik}$ $\quad \overset{2}{\beta}_{ik}=\beta'_{ik}$

The approximate solution corresponding to $\overset{0}{\delta}_n$ is $x_n=\sum_{k=1}^{n}a_k e_k$, where $a_n=\frac{b_n}{\beta_{nn}}$, $a_i=\frac{b_i}{\beta_{ii}}-$

$\bar{\gamma}_{ik}$ is the complex number conjugated to γ_{ik}.

The small numbers in the corners indicate the order in which the computations should be

$\breve{\bar{\gamma}}_{31}\breve{\beta}_{31}-\breve{\bar{\gamma}}_{32}\breve{\beta}_{32}$				
$\breve{\bar{\gamma}}_{31}\breve{\beta}_{41}-\breve{\bar{\gamma}}_{32}\breve{\beta}_{42}$	[19] $\breve{\beta}_{44}=\breve{\alpha}_{44}-\breve{\bar{\gamma}}_{41}\breve{\beta}_{41}-\breve{\bar{\gamma}}_{42}\breve{\beta}_{42}-\breve{\bar{\gamma}}_{43}\breve{\beta}_{43}$			
. . . . .	. . . . .	. . .		
$\breve{\bar{\gamma}}_{31}\breve{\beta}_{k1}-\breve{\bar{\gamma}}_{32}\breve{\beta}_{k2}$	$\breve{\beta}_{k4}=\breve{\alpha}_{k4}-\breve{\bar{\gamma}}_{41}\breve{\beta}_{k1}-\breve{\bar{\gamma}}_{42}\breve{\beta}_{k2}-\breve{\bar{\gamma}}_{43}\breve{\beta}_{k3}$ $\breve{\gamma}_{k4}=\frac{1}{\breve{\beta}_{44}}\breve{\beta}_{k4}$	. . . . . .	$\breve{\beta}_{kk}=\breve{\alpha}_{kk}-\sum_{i=1}^{k-1}\breve{\bar{\gamma}}_{ki}\breve{\beta}_{ki}$	
. . . . .	. . . . .	. . .	. . . . .	. . .
$\breve{\bar{\gamma}}_{31}\breve{\beta}_{n1}-\breve{\bar{\gamma}}_{32}\breve{\beta}_{n2}$	$\breve{\beta}_{n4}=\breve{\alpha}_{n4}-\breve{\bar{\gamma}}_{41}\breve{\beta}_{n1}-\breve{\bar{\gamma}}_{42}\breve{\beta}_{n2}-\breve{\bar{\gamma}}_{43}\breve{\beta}_{n3}$ $\breve{\gamma}_{n4}=\frac{1}{\breve{\beta}_{44}}\breve{\beta}_{n4}$	. . . . . .	$\breve{\beta}_{nk}=\breve{\alpha}_{nk}-\sum_{i=1}^{k-1}\breve{\bar{\gamma}}_{ki}\breve{\beta}_{ni}$ $\breve{\gamma}_{nk}=\frac{1}{\breve{\beta}_{kk}}\breve{\beta}_{nk}$	. . . . . .	$\breve{\beta}_{nn}=\breve{\alpha}_{nn}-\sum_{i=1}^{n-1}\breve{\bar{\gamma}}_{ni}\breve{\beta}_{ni}$

$\gamma_{ki}a_k$ for $i=n-1, n-2, \ldots, 2, 1.$

ied out.

Let us assume that for $k=n$ we have $\|x'_n\|^2-\|x_n\|^2=\delta'_n-\delta_n<\varepsilon$. Then we find the suitable approximate solution x_n in the form $x_n=\sum_{k=1}^{n} a_k e_k$ as in [1], where

$$a_n=\frac{\overline{b}_n}{\beta_{nn}}; \qquad a_i=\frac{\overline{b}_i}{\beta_{ii}}-\sum_{k=i+1}^{n}\gamma_{ki}a_k \qquad \text{for} \qquad i=n-1,n-2,\ldots,2,1.$$

The above method and the reckoning scheme can be applied to find the approximate solutions of linear equations by the well-known method of orthogonal projection developed by H. Weyl [3] and generalised by M. I. Višik [4]. The above method is also applicable to Trefftz's method generalised by K. Maurin [5].

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MATHEMATICS

Use of Expansions with a Negative Basis in the Arithmometer of a Digital Computer

by

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In designing a modern automatic digital computer it is important to obtain a possibly uniform organisation of the machine. This not only gives a clearer scheme but also helps to eliminate some of the defective actions, improves the control and even simplifies the process of constructing such a machine. The present paper contains a suggestion of a more uniform conception of the arithmetical unit of a digital computer. Similar investigations, though for a different purpose, have been made by Shannon [1].

In the arithmetical units of the digital computers so far constructed, many complications, with regard both to organisation and to the technical aspect, are due to the necessity of performing the basic arithmetical operations (addition, subtraction, multiplication and division) on numbers with both signs. This is connected with the practice of representing negative numbers in arithmetical unit either as a system of digits with a sign (I B M-701, BARK) or by means of a complement (ENIAC, EDSAC). In effect, it is necessary to perform one algorithm on signs and another on numbers, or to perform complicated and non-uniform algorithms.

The method suggested here eliminates this inconvenience by introducing expansions of numbers with a negative basis. As in the case of a positive basis, an expansion of a real number with an integer basis $g<-1$ is what we call the series

$$\alpha = \sum_{i=-\infty}^{m} c_i g^i,$$

m — being an integer and c_i a natural number satisfying the inequality

$$0 \leqslant c_i \leqslant -g-1, \quad i- \text{ an integer}, \quad -\infty < i \leqslant m.$$

It is easy to prove the following theorems on expansions with a negative basis.

THEOREM 1. *Every real number has an expansion with the integer basis* $g<-1$.

THEOREM 2. *If a number has a finite expansion, that expansion is unique.*

THEOREM 3. *Expansions of real numbers with the integer basis* $g<-1$ *are unique, with the exception of numbers* a *of the form*

$$a=E\frac{g^k}{(-g+1)}+C\cdot g^{k+1},$$

where $E=\pm 1$ *and* C *and* k *are any integers. These numbers have two distinct infinite expansions.*

On the basis of these theorems we can formulate the algorithms of the basic arithmetical operations on expansions of numbers with an integer negative basis. Since most arithmetical units of existing digital computers compute on expansions with the basis 2, we shall confine ourselves to giving the algorithms of operations on expansions with the basis -2, which, moreover, will facilitate to some extent the comparison of the method here presented with those hitherto applied. It should be observed, however, that it presents no difficulties to arrive at analogous algorithms for expansions with any integer basis $g<-1$.

Algorithms of basic operations

Let us take two numbers: $\alpha=\sum_{i=-n_1}^{m_1} a_i(-2)^i$, $\beta=\sum_{i=-n_2}^{m_2} b_i(-2)^i$. Let their sum be $\alpha+\beta=\gamma$, $\gamma=\sum_{i=-n_3}^{m_3} c_i(-2)^i$, where n_j, m_j are non-negative integers $(j=1,2,3)$ and $a_i, b_i, c_i=0,1$.

The carry p_j, which occurs in adding two digits, a_j and b_j, will be defined in the same way as in the case of a positive basis:

$$c_j+p_j(-2)=a_j+b_j+p_{j-1}.$$

The above iteration formula obviously gives for p_j the values 0, 1 and -1. This observation makes it possible to arrange the following addition table:

a_j	0	0	1	1	0	0	1	1	0	0	1	1
b_j	0	1	0	1	0	1	0	1	0	1	0	1
p_{j-1}	0	0	0	0	1	1	1	1	-1	-1	-1	-1
c_j	0	1	1	0	1	0	0	1	1	0	0	1
p_j	0	0	0	-1	0	-1	-1	-1	1	0	0	0

This algorithm is more complicated than the algorithm for the sum of two positive numbers but, on the whole, not more difficult than the normal one, in which we must perform the operations on signs separately. Its advantage is that it treats all places in a number in the same way.

The algorithm of subtraction is easily reduced to addition by the formula

$$a-b=a+b+(-2)b,$$

which is easy to carry out, for it is obvious that $(-2)\ b$ is a shifting of number b one place to the left. For a number opposite to a we can give a similar formula:

$$-a=a+(-2)a.$$

Of course, this method of carrying out subtraction is not always useful (e. g., in working with machines having fixed points). However, listing a subtraction table is as easy as in the case of addition with a negative basis.

We have already mentioned that multiplication, by the basis, of an expanded number with the basis -2 results in its shifting one place to the left. It follows that the algorithm of multiplying numbers with the negative basis -2 is identical with multiplying positive numbers by the basis 2, provided the addition is performed according to the algorithm given at the beginning.

We shall now give the algorithm of division, which presents a different idea from the normal ones. With regard to the use of algorithms with a negative basis we wish to simplify as much as possible the method of investigating the remainder in division.

We define α and β as above. Write

$$N(\alpha)=\max[a_{n_1}\cdot 2^{-n_1},\ldots,a_i 2^i,\ldots,a_{m_1}2^{m_1}] \quad \text{and} \quad \alpha_k=(-2)^k\cdot\alpha.$$

The initial value of the subtracted divisor α_p is found from the relation $N(\beta)=N(\alpha_p)$. The algorithm of forming the quotient β: $\alpha=w=\sum_{i=p} w_i$ is found by defining w_l in the following way:

1° Perform the subtraction

$$v_l-\alpha_k=v_{l+1},$$

where

$$v_p=\beta.$$

a) If $N(v_{l+1})>N(\alpha_k)$, then $w_k=0$; we must then replace k by $k-1$ and perform 1°.

b) If $N(v_{l+1})=N(\alpha_k)$, then $w_k=(-2)^k$; we must perform 1° replacing i by $i+1$.

c) If $N(v_{l+1})<N(v_l)$, then $w_k=+(-2)^k$; we must then replace k by $k-1$ and i by $i+1$, and perform 1°.

This algorithm, although fairly complicated, does not seem more difficult to realise than those normally used.

Final remarks

There are a few small points that should also be observed with regard to the negative basis. In the present systems of representing numbers in the machine, the appearance of two zeros has often been very troublesome (e. g., $+0$ and -0 or 1.111111... and 0.00000). In the system which we are suggesting there exists only one 0. Consequently the elimination of one of the zeros causes that, for the fixed numerical interval (e. g., $|x|<1$), the zero is not its centre but divides it in relation 2:1. However, the asymmetry with respect to zero does not seem to be a drawback of our principle.

It will be observed, moreover, that the greatest advantage of the proposed principle of expanding numbers in a digital computer is the avoidance of the necessity of performing some operations on digits and other operations on signs; consequently, we avoid in the arithmometer any information of the nature of incoming symbols, which is a great drawback of realisations in series. In effect, we can reduce the number of systems with different actions in the arithmetic unit.

The use of expansions with a negative basis makes it possible to record real numbers solely with the aid of signs which are interpreted as digits.

In the principle here proposed the algorithm of multiplication is distinctly better, other algorithms do not seem more difficult than those normally used. However, they are all built on a uniform idea, which implies a simplification of the logical scheme of the machine and makes for a reduced probability of an incorrect action. This involves better control — "manual" or automatic — of the performance of the arithmetic unit.

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MATHEMATICS

A Limit Theorem for *a posteriori* Distributions

by

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Presented by H. STEINHAUS on December 14, 1956

Assume given a compact topological space $\mathfrak{X}$ and let m be a completely additive measure defined on the field of Borel subsets of $\mathfrak{X}$, such that

$$m(A)>0 \tag{1}$$

for every open non-empty set $A\subset\mathfrak{X}$. We shall denote by $\mathfrak{F}$ a space of *density functions*, i. e., a space of continuous functions f defined on $\mathfrak{X}$ and satisfying the following conditions:

$$f(x)>0 \quad \text{for} \quad x\in\mathfrak{X}, \quad \int_{\mathfrak{X}} f(x)\,m(dx)=1. \tag{2}$$

We assume that $\mathfrak{F}$ is compact with respect to the norm $\|f\|=\max_{x\in\mathfrak{X}}|f(x)|$ and contains at least two elements. Let Γ_{f_0} ($f_0\in\mathfrak{F}$) be a class of *a priori distributions*, i. e., a class of completely additive normed measures γ defined on the field of Borel subsets of $\mathfrak{F}$ and satisfying for each neighbourhood V of f_0 the inequality

$$\gamma(V)>0. \tag{3}$$

We shall denote by δ_{f_0} the measure defined by the formula

$$\delta_{f_0}(U)=\begin{cases}1 & \text{if} \quad f_0\in U\\ 0 & \text{if} \quad f_0\overline{\in} U\end{cases} \quad (U\subset\mathfrak{F}).$$

The mean information for discrimination between f_0 and f ($f_0,f\in\mathfrak{F}$) is given by the formula

$$I_{f_0}(f)=\int_{\mathfrak{X}} f_0(x)\log\frac{f_0(x)}{f(x)}\,m(dx)$$

(cf. [3], pp. 18, 19; [4], p. 76). The inequality (1) implies

$$I_{f_0}(f)>0 \quad \text{for} \quad f\neq f_0 \tag{4}$$

(cf. [2], p. 82). Put

$$I_{f_0}(U)=\inf_{f\in U} I_{f_0}(f) \qquad (U\subset\mathcal{F}). \tag{5}$$

Since $\mathcal{F}$ is compact, the inequality (4) implies

$$I_{f_0}(U)>0 \quad \text{if} \quad f_0\,\bar{\in}\,\overline{U}, \tag{6}$$

$$I_{f_0}(U)=0 \quad \text{if} \quad f_0\in\overline{U}, \tag{7}$$

($\overline{U}$ denotes the closure of U).

Let $\langle\Omega, Pr\rangle$ be a probability space, i. e., Ω is a space of elementary events and "Pr" a probability measure defined on a field of subsets of Ω. Let us consider a sequence $X_1(\omega), X_2(\omega), \ldots$ $(\omega\in\Omega)$ of independent $\mathcal{X}$-valued random variables with the common distribution $Pr\{X_k(\omega)\in A\}=\int_A f_0(x)m(dx)$ $(k=1,2,\ldots)$.

Suppose that the density function f_0 is unknown and γ $(\gamma\in\Gamma_{f_0})$ is the *a priori* distribution of this density function. Then the *a posteriori distribution* founded on the system $X_1(\omega), X_2(\omega), \ldots, X_n(\omega)$ is given by the formula

$$\mu_n^{(\gamma)}(U,\omega)=\frac{\int_U \prod_{k=1}^{n} f(X_k(\omega))\gamma(df)}{\int_{\mathcal{F}} \prod_{k=1}^{n} f(X_k(\omega))\gamma(df)}, \tag{8}$$

where U is a Borel subset of $\mathcal{F}$.

The purpose of this note is to prove the following theorem, which we believe to be new.

THEOREM. *For almost every $\omega\in\Omega$ the relation*

$$\lim_{n\to\infty}\left(\mu_n^{(\gamma)}(U,\omega)-\delta_{f_0}(U)\right)\exp\left(n\lambda I_{f_0}(U)\right)=0 \tag{9}$$

*holds for each $\gamma\in\Gamma_{f_0}$, $\lambda<1$ and for each Borel set U $(U\subset\mathcal{F})$, such that $f_0\,\bar{\in}\,\mathrm{Fr}(U)$ *).*

Moreover, for each $\lambda>1$ there exists a $\gamma_0\in\Gamma_{f_0}$ such that

$$\lim_{n\to\infty}\left(\mu_n^{(\gamma_0)}(U,\omega)-\delta_{f_0}(U)\right)\exp\left(n\lambda I_{f_0}(U)\right)=\infty \tag{10}$$

for some Borel set U $(U\subset\mathcal{F})$, $f_0\,\bar{\in}\,\mathrm{Fr}(U)$ and for almost every $\omega\in\Omega$.

Proof. Let U be a Borel subset of $\mathcal{F}$ and $f_0\,\bar{\in}\,\overline{U}$. Suppose

$$\lambda<1. \tag{11}$$

Since the inequalities (2), (6), (11) hold, and $\mathcal{X}$, $\mathcal{F}$ are compact, there is a decomposition $\mathcal{X}=\mathcal{X}_1\cup\mathcal{X}_2\cup\ldots\cup\mathcal{X}_s$, where $\mathcal{X}_j$ $(j=1,2,\ldots,s)$ are

*) $\mathrm{Fr}(U)$ denotes the boundary of U.

disjoint Borel sets and for each $f \in \mathcal{F}$

$$|\log f(x') - \log f(x'')| < \frac{1-\lambda}{10} I_{f_0}(U) \quad \text{if} \quad x', x'' \in \bar{\mathcal{X}}_j \ (j=1,2,\ldots,s). \tag{12}$$

Since $\mathcal{X}$ and $\mathcal{F}$ are compact, the inequality (2) implies

$$M = \max_{x \in \mathcal{X}, f \in \mathcal{F}} |\log f(x)| < \infty. \tag{13}$$

χ_j will denote the characteristic function of a set $\mathcal{X}_j$ $j=1,2,\ldots,s$. According to the strong law of large numbers (cf. for example, [1], pp. 464, 465),

$$\lim_{n\to\infty} \frac{1}{n} \sum_{k=1}^{n} \chi_j(X_k(\omega)) = \int_{\mathcal{X}_j} f_0(x)\, m(dx) \qquad (j=1,2,\ldots,s)$$

for $\omega \in \Omega_0$, where $Pr\{\Omega_0\}=1$. Let $n_0(\omega)$ be an integer, such that for $n \geqslant n_0(\omega)$ the inequality

$$\left| \frac{1}{n} \sum_{k=1}^{n} \chi_j(X_k(\omega)) - \int_{\mathcal{X}_j} f_0(x)\, m(dx) \right| < \frac{1-\lambda}{10 s M} I_{f_0}(U) \qquad (j=1,2,\ldots,s; \quad \omega \in \Omega_0) \tag{14}$$

is true. Put

$$\begin{aligned} a_f^{(j)} &= \min_{x \in \bar{\mathcal{X}}_j} \log f(x) \\ b_f^{(j)} &= \max_{x \in \bar{\mathcal{X}}_j} \log f(x) \end{aligned} \qquad (j=1,2,\ldots,s; \quad f \in \mathcal{F}).$$

The inequalities (12), (13) and (14) imply

$$\begin{aligned} &\left| \frac{1}{n} \sum_{j=1}^{s} a_f^{(j)} \sum_{k=1}^{n} \chi_j(X_k(\omega)) - \int_{\mathcal{X}} f_0(x) \log f(x)\, m(dx) \right| \\ &\leqslant \sum_{j=1}^{s} |a_f^{(j)}| \left| \frac{1}{n} \sum_{k=1}^{n} \chi_j(X_k(\omega)) - \int_{\mathcal{X}_j} f_0(x)\, m(dx) \right| \\ &\quad + \sum_{j=1}^{s} \int_{\mathcal{X}_j} |a_f^{(j)} - \log f(x)|\, f_0(X)\, m(dx) < \frac{1-\lambda}{5} I_{f_0}(U) \end{aligned} \tag{15}$$

for $\omega \in \Omega_0$, $n \geqslant n_0(\omega)$ and $f \in \mathcal{X}$. In the same way we obtain

$$\left| \frac{1}{n} \sum_{j=1}^{s} b_f^{(j)} \sum_{k=} \chi_j(X_k(\omega)) - \int_{\mathcal{X}} f_0(x) \log f(x)\, m(dx) \right| < \frac{1-\lambda}{5} I_{f_0}(U) \tag{16}$$

for $\omega \in \Omega_0$, $n \geqslant n_0(\omega)$ and $f \in \mathcal{F}$.

It is easy to verify the following inequalities:

$$\exp\Big(\sum_{j=1}^{s} a_f^{(j)} \sum_{k=1}^{n} \chi_j(X_k(\omega))\Big) \leqslant \prod_{k=1}^{n} f(X_k(\omega)) \leqslant \exp\Big(\sum_{j=1}^{s} b_f^{(j)} \sum_{k=1}^{n} \chi_j(X_k(\omega))\Big).$$

Hence, in view of (15) and (16),

$$\exp\Big(n\int_{\mathfrak{X}} f_0(x)\log f(x)\,m(dx) - n\frac{1-\lambda}{5} I_{f_0}(U)\Big) \tag{17}$$

$$< \prod_{k=1}^{n} f(X_k(\omega)) < \exp\Big(n\int_{\mathfrak{X}} f_0(x)\log f(x)\,m(dx) + n\frac{1-\lambda}{5} I_{f_0}(U)\Big)$$

for $\omega \in \Omega_0$, $n \geqslant n_0(\omega)$ and $f \in \mathcal{F}$. Since for $f \in U$

$$\int_{\mathfrak{X}} f_0(x)\log f(x)\,m(dx) = \int_{\mathfrak{X}} f_0(x)\log f_0(x)\,m(dx) - I_{f_0}(f)$$

$$\leqslant \int_{\mathfrak{X}} f_0(x)\log f_0(x)\,m(dx) - I_{f_0}(U),$$

the formula (17) implies

$$\prod_{k=1}^{n} f(X_k(\omega)) \leqslant \exp\Big(n\int_{\mathfrak{X}} f_0(x)\log f_0(x)\,m(dx) - n\frac{4+\lambda}{5} I_{f_0}(U)\Big) \tag{18}$$

for $\omega \in \Omega_0$, $n \geqslant n_0(\omega)$ and $f \in U$.

Let U_0 be a neighbourhood of f_0, such that

$$\Big|\int_{\mathfrak{X}} f_0(x)\log f(x)\,m(dx) - \int_{\mathfrak{X}} f_0(x)\log f_0(x)\,m(dx)\Big| < \frac{1-\lambda}{10} I_{f_0}(U)$$

for $f \in U_0$. Then, in view of (17),

$$\prod_{k=1}^{n} f(X_k(\omega)) \geqslant \exp\Big(n\int_{\mathfrak{X}} f_0(x)\log f_0(x)\,m(dx) - n\frac{3(1-\lambda)}{10} I_{f_0}(U)\Big) \tag{19}$$

for $\omega \in \Omega_0$, $n \geqslant n_0(\omega)$ and $f \in U_0$. From (8), (18) and (19) it follows that

$$0 \leqslant \big(\mu_n^{(\gamma)}(U,) - \delta_{f_0}(U)\big)\exp\big(n\lambda I_{f_0}(U)\big)$$

$$\leqslant \frac{\int_U \prod_{k=1}^{n} f(X_k(\omega))\,\gamma(df)}{\int_{U_0} \prod_{k=1}^{n} f(X_k(\omega))\,\gamma(df)} \exp\big(n\lambda I_{f_0}(U)\big)$$

$$\leqslant \frac{\gamma(U)}{\gamma(U_0)} \exp\Big(n\frac{\lambda-1}{2} I_{f_0}(U)\Big)$$

for $\omega \in \Omega_0$, $n \geqslant n_0(\omega)$. Hence, according to (3), (6) and (11) the equality (9) holds for $\omega \in \Omega_0$, $\gamma \in \Gamma_{f_0}$, $\lambda < 1$ and for each Borel set U, such that $f_0 \in \overline{U}$.

If f_0 belongs to the interior of U, then $f_0 \in \overline{\mathcal{F}-U}$ and, in view of (7) and (8),

$$\left(\mu_n^{(\gamma)}(U,\omega)-\delta_{f_0}(U)\right)\exp\left(n\lambda I_{f_0}(U)\right)=\mu_n^{(\gamma)}(\mathcal{F}-U,\omega)\to 0$$

for $\omega \in \Omega_0$ and $\gamma \in \Gamma_{f_0}$. The first part of the theorem is thus proved.

Suppose $\lambda_0>1$. We define the *a priori* distribution $\gamma_0 \in \Gamma_{f_0}$ by the following formulae: $\gamma_0(\{f_0\})=2^{-1}$, $\gamma_0(\{f_1\})=2^{-1}$ and $\gamma_0(V)=0$ if $f_0, f_1 \notin V$, where $f_0 \neq f_1$.

Putting $U=\{f_1\}$, we have

$$\left(\mu_n^{(\gamma_0)}(U,\omega)-\delta_{f_0}(U)\right)\exp\left(n\lambda_0 I_{f_0}(U)\right)= \tag{20}$$

$$=\left[\exp\left(-n\lambda_0 I_{f_0}(U)\right)+\left(\prod_{k=1}^{n}\frac{f_0(X_k(\omega))}{f_1(X_k(\omega))}\right)\exp\left(-n\lambda_0 I_{f_0}(U)\right)\right]^{-1}.$$

According to the inequality (17) (for $\lambda>1-\frac{1}{2}(\lambda_0-1)$) the sequence

$$\prod_{k=1}^{n}\frac{f_0(X_k(\omega))}{f_1(X_k(\omega))}\exp\left(-n\lambda_0 I_{f_0}(U)\right.$$

converges to 0 for $\omega \in \Omega_0$. Consequently, in view of (20), we obtain (10) for $U=\{f_1\}$. The theorem is thus proved.

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БЮЛЛЕТЕНЬ
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МАТЕМАТИКА

В. БОГДАНОВИЧ

СЛАБАЯ НЕПРЕРЫВНОСТЬ ПОЛИНОМНЫХ ФУНКЦИОНАЛОВ НА ПРОСТРАНСТВЕ c_0

Представлено С. МАЗУРОМ 14 декабря 1956

В настоящей работе содержится ответ на один из вопросов, поставленных профессором С. Мазуром в 1955 году в связи с результатами, касающимися непрерывности полиномных функционалов на некоторых линейных пространствах со специальной топологией, которые своевременно получил А. Пэлчинский.

Условимся называть функционал $\varphi(x)$ — определенный на линейном топологическом пространстве E — линейным, если он непрерывен и при произвольных числах t_1, t_2 и x_1, $x_2 \in E$ удовлетворяет равенству

$$\varphi(t_1 x_1 + t_2 x_2) = t_1 \varphi(x_1) + t_2 \varphi(x_2)$$

В пространствах Банаха при помощи линейных функционалов определяется слабая топология. Именно последовательность точек x_n называется слабо сходящейся к точке x_0, если для всякого функционала φ линейного на этом пространстве последовательность $\varphi(x_n)$ сходится к $\varphi(x_0)$. Функционал $\varphi^k(x_1, x_2, \ldots, x_k)$ определенный на произведении $\underbrace{E \times E \times \ldots \times E}_{k} = E^k$, где E линейное топологическое пространство, называется k-линейным на E, если он непрерывен на E^k и линеен по каждой переменной при фиксированных остальных переменных. Полиномным функционалом на E называется всякий функционал, представимый в форме

$$\varphi(x) = \sum_{k=1}^{r} \varphi^k(x, x \ldots x),$$

где $\varphi^k(x_1, x_2, \ldots, x_k)$ — k-линейный функционал на пространстве E.

Обозначим через c_0 линейное пространство всех числовых последовательностей, сходящихся к нулю. Это пространство является пространством Банаха, если в нем определить норму $\|x\|$ элемента $x = (t_m) \in c_0$ как $\sup |t_m|$. При этом последовательность точек $x_n \in c_0$ слабо сходится в c_0 к точке $x_0 \in c_0$ тогда и только тогда, когда выполняются условия

$$\sup_{n,m=1,2\ldots} |t_m^n| < \infty, \tag{1}$$

$$\lim_n t_m^n = t_m^0, \quad \text{для} \quad m=1,2,\dots, \tag{2}$$

где, $(t_m^n)=x_n$ для $n=0,1,2,\dots$ Линейное пространство всех ограниченных числовых последовательностей со следующей топологией $x_n \to x_0$, где $x_n=(t_m^n)$ для $n=0,1,2,\dots,$ тогда и только тогда, когда выполняются условия (1) и (2), обозначим через m^*.

Докажем следующую теорему:

Теорема 1. *Каждый функционал $\varphi(x_1,x_2,\dots,x_k)$ k-линейный на пространстве c_0 продолжается и притом лишь единственным способом, к функционалу φ^* k-линейному на пространстве m^*.*

В доказательстве используем следующую теорему Шура: *Если для всякой ограниченной последовательности t_m и $n=1,2,3,\dots$ ряд*

$$\sum_{m=1}^{\infty} a_{n,m} t_m$$

сходится и существует предел

$$\lim_n \sum_{m=1}^{\infty} a_{n,m} t_m,$$

то ряд

$$\sum_{m=1}^{\infty} |a_{n,m}| \quad \text{для} \quad n=1,2,3,\dots$$

сходится равномерно.

Доказательство нашей теоремы проведем по индукции. Положим

$$e_l=(\delta_m^l);\ \delta_m^l=\begin{cases} 1 & \text{для} \quad m=l \\ 0 & \text{для} \quad m\neq l \end{cases} \qquad l,m=1,2,3,\dots$$

Тогда каждый элемент $x=(t_m)\in c_0$ представим как сумма ряда

$$x=\sum_{m=1}^{\infty} t_m e_m$$

сходящегося в смысле сходимости по норме в пространстве c_0. Для $k=1$ получаем

$$\varphi(x)=\sum_{m=1}^{\infty}\varphi(e_m)t_m, \quad \text{где} \quad x=(t_m)\in c_0 \quad \text{и} \quad \sum_{m=1}^{\infty}|\varphi(e_m)|<\infty.$$

Поэтому функционал

$$\varphi^*(y)=\sum_{m=1}^{\infty}\varphi(e^m)t_m \quad \text{для} \quad y=(t_m)\in m^*$$

является, как легко установить, требуемым продолжением функционала φ на

пространство m^*. Так как множество $c_0 \subset m^*$ плотное в пространстве m^*, это продолжение единственно.

Пусть теорема доказана для k-линейных функционалов и пусть $\varphi(x_1,\ldots,x_k,x_{k+1})$ будет $k+1$-линейным функционалом на пространстве c_0.

Пусть $\varphi_m(y_1,\ldots,y_k)$ будет продолжением на пространство m^* функционала $\varphi(x_1,\ldots,x_k,e_m)$.

Так как

$$\varphi(x_1,\ldots,x_k,x_{k+1})=\sum_{m=1}^{\infty}\varphi_m(x_1,\ldots,x_k)t_m$$

для $x_1,\ldots,x_k\in c_0$ и $x_{k+1}=(t_m)\in c_0$, то функционал

$$\psi(x_1,\ldots,x_k,y_{k+1})=\sum_{m=1}^{\infty}\varphi_m(x_1,\ldots,x_k)\,t_m,$$

где $x_1,\ldots,x_k\in c_0$ и $y_{k+1}=(t_m)\in m^*$, является хорошо определеннным и при фиксированном y_{k+1}, как предел последовательности k-линейных функционалов, по известной теореме Банаха, сам является k-линейным функционалом по переменным $x_1,\ldots,x_k$. Возьмем произвольные $y_1,\ldots,y_k,y_{k+1}\in m^*$ и последовательности точек $x_1^n,\ldots,x_k^n,x_{k+1}^n\in c_0$, сходящиеся в смысле сходимости в пространстве m^* соответственно к точкам $y_1,\ldots,y_k,y_{k+1}$. При произвольном $y_{k+1}=(t_m)\in m^*$ последовательность

$$\psi(x_1^n,\ldots,x_k^n,y_{k+1})=\sum_{m=1}^{\infty}\varphi_m(x_1^n,\ldots,x_k^n)\,t_m$$

сходится, так как при фиксированном y_{k+1} k-линейный функционал по предположению продолжается к некоторому функционалу $\psi^*(y_1,\ldots,y_k)$ k-линейному на пространстве m^* и, поэтому

$$\psi(x_1^m,\ldots,x_k^m,y_{k+1})=\psi^*(x_1^n,\ldots,x_k^n)\to\psi^*(y_1,\ldots,y_k).$$

Следовательно, по теореме Шура, ряд

$$\sum_{m=1}^{\infty}|\varphi_m(x_1^n,\ldots,x_k^n)|$$

сходится равномерно для $n=1,2,3,\ldots$

Поэтому вполне обоснован следующий предельный переход

$$\text{(A)}\qquad \lim_n\varphi(x_1^n,\ldots,x_k^n,x_{k+1}^n)=\lim_n\sum_{m=1}^{\infty}\varphi_m(x_1^n,\ldots,x_k^n)t_m^n=\sum_{m=1}^{\infty}\varphi_m(y_1,\ldots,y_k)t_m$$

$\left((t_m^n)=x_{k+1}^n,(t_m)=y_{k+1}\right)$, а тем самым продолжение функционала φ на пространство m^*

$$\varphi^*(y_1,\ldots,y_k,y_{k+1})=\sum_{m=1}^{\infty}\varphi_m(y_1,\ldots,y_k)t_m$$

является хорошо определенным.

Все требуемые свойства для того, чтобы φ^* был $k+1$-линейным функционалом, кроме непрерывности, очевидны. Поэтому достаточно доказать, что для произвольных ограниченных последовательностей $y_1^n, \dots y_{l+1}^n, y_{l+1}^n, \dots, y_{k+1}^n$ (последовательность $y^n=(t_m^n)$ ограничена, если $\sup_{n,m}|t_m^n|<\infty$) и последовательности y_l^n, сходящейся в смысле сходимости в пространстве m^* к нулю, последовательность

$$\varphi^*(y_1^n, \dots, y_{l-1}^n, y_l^n, y_{l+1}^n, \dots, y_{k+1}^n)$$

стремится к нулю. Из определения функционала φ^* и из равенства (A) следует существование таких ограниченных последовательностей $x_1^n, \dots, x_{k+1}^n \in c_0$, что

$$|\varphi^*(y_1^n, \dots, y_{k+1}^n)-\varphi^*(x_1^n, \dots, x_{k+1}^n)|<\frac{1}{n} \quad \text{для} \quad n=1,2,3,\dots,$$

при этом если последовательность y_l^n сходится к нулю, то можно так подобрать последовательность x_l^n, чтобы она тоже сходилась к нулю. Поэтому достаточно доказать, что для ограниченных последовательностей $x_1^n, \dots, x_{l-1}^n, x_{l+1}^n, \dots, x_{k+1}^n$ и последовательности $x_l^n \in c_0$, слабо сходящейся к нулю в пространстве c_0, последовательность

$$\varphi^*(x_1^n, \dots, x_{l-1}^n, x_l^n, x_{l+1}^n, \dots, x_{k+1}^n)=\varphi(x_1^n, \dots, x_{l-1}^n, x_l^n, x_{l+1}^n, \dots, x_{k+1}^n)$$

стремится к нулю. Но это доказывается по индукции, применением метода подобного тому, которым мы доказали обоснованность предельного перехода (A).

Единственность функционала φ^* следует из равенства (A).

Замечание. Мы доказали даже больше чем непрерывность, а именно мы доказали, что из условия: $y_i^n-\bar{y}_i^n \to 0$ для $i=1,2,\dots,k+1$, следует, что

$$\varphi^*(y_1^n, \dots, y_{k+1}^n)-\varphi^*(\bar{y}_1^n, \dots, \bar{y}_{k+1}^n) \to 0,$$

а это есть равномерная непрерывность

Слабая равномерная непрерывность полиномных функционалов на пространстве c_0 сразу вытекает из самого их определения.

МАТЕМАТИЧЕСКИЙ ИНСТИТУТ ПОЛЬСКОЙ АКАДЕМИИ НАУК

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MATHEMATICS

On Singular Integrals

by

W. BOGDANOWICZ

Presented by S. MAZUR on December 14, 1956

The present note contains a necessary and sufficient condition that the sequence of singular integrals

$$\text{(A)} \qquad \int_a^b \alpha_n(s,t)x(t)\,dt$$

for every function $x(t)$ belonging to L^p be convergent to its value $x(s)$:

1) at all points s which are its Lebesgue points;

2) at all points s at which

$$\text{(B)} \qquad x(s)=\lim_{h\to 0} h^{-1}\int_s^{s+h} x(t)\,dt.$$

Denote by L^p the space of functions, measurable in the interval (a,b) such that $\int_a^b |x(t)|^p\,dt<\infty (p\geqslant 1)$, with the norm

$$\|x\|=\Big(\int_a^b |x(t)|^p\,dt\Big)^{1/p},$$

and by M the space of functions essentially bounded with the norm

$$\|x\|=\operatorname*{ess\,sup}_{t\in(a,b)} |x(t)|.$$

Let Φ_s, Γ_s denote, respectively, the spaces of functions measurable in the interval $\langle a,b\rangle$ for which the integral

$$\int_a^s \operatorname*{ess\,sup}_{v\in(a,t)} |x(v)|\,dt+\int_s^b \operatorname*{ess\,sup}_{v\in(t,b)} |x(v)|\,dt$$

has a finite value and the space of real functions for which the integral

$$\int_a^s \operatorname*{var}_{v\in\langle a,t\rangle} x(v)\,dt+\int_s^b \operatorname*{var}_{v\in\langle t,b\rangle} x(v)\,dt$$

has a finite value. The values of these integrals are accepted as the norm of the element x.

Let $a_n(s,t)$ be a sequence of functions measurable with respect to t in the interval $\langle a,b\rangle$ with any fixed s belonging to the interval $\langle a,b\rangle$.

THEOREM 1. *The sequence of integrals* (A) *tends, for every function* $x \in L^p$, *to its value* $x(s)$ *at all points* s *which are its Lebesgue points if, and only if, the following conditions are satisfied for any* s *belonging to* $\langle a,b\rangle$:

(1) $\lim\limits_{n} \int\limits_{a}^{b} a_n(s,t)\,dt = 1$;

(2) $\lim\limits_{n} \int\limits_{c}^{d} a_n(s,t)\,dt = 0$ *for every closed interval* $\langle c,d\rangle \subset \langle a,b\rangle$ *that does not contain the point* s;

(3) *there exists* n_s *such that:*

for $p=1$ *there exist a* K *and a sequence* $\varphi_n^s \in \Phi_s$ *such that* $a_n(s,t)=\varphi_n^s(t)$ *almost everywhere in* (a,b) *for* $n>n_s$,

$$\|\varphi_n^s\| < K \quad \text{for} \quad n > n_s;$$

for $p>1$ *a* K *and sequences* $\varphi_n^s \in \Phi_s$, $\beta_n^s \in L^q\left(\frac{1}{p}+\frac{1}{q}=1\right)$ *exist, such that* $a_n(s,t)=\varphi_n^s(t)+\beta_n^s(t)$ *almost everywhere in* (a,b) *for* $n>n_s$,

$$\|\varphi_n^s\| < K, \ \|\beta_n^s\| < K \quad \text{for} \quad n > n_s.$$

THEOREM 2. *The sequence of integrals* (A) *for every function* $x \in L^p$ *tends to its value* $x(s)$ *at all points* s *at which condition* (B) *holds if, and only if, for any* $s \in \langle a,b\rangle$, *conditions* 1 *and* 2 *from Theorem* 1 *and the following conditions are satisfied:*

there exists n_s *such that:*

for $p=1$ *a* K *and sequences* $\gamma_n^s \in \Gamma_s$, $\beta_n^s \in M$ *exist, such that* $a_n(t,s)=\gamma_n^s(t)+\beta_n^s(t)$ *almost everywhere in* (a,b) *for* $n>n_s$,

$$\|\gamma_n^s\| < K, \ \|\beta_n^s\| < K \quad \text{for} \quad n > n_s;$$

for $p>1$ *a* K *and sequences* $\gamma_n^s \in \Gamma_s$, $\beta_n^s \in L^q\left(\frac{1}{p}+\frac{1}{q}=1\right)$ *exist, such that* $a_n(s,t)=\gamma_n^s(t)+\beta_n^s(t)$ *almost everywhere in* (a,b) *for* $n>n_s$,

$$\|\gamma_n^s\| < K, \ \|\beta_n^s\| < K \quad \text{for} \quad n > n_s.$$

Denote by Γ the space of all functions $x(t)$ continuous to the right in the interval $(0,1\rangle$ and equal to zero at the point 1, for which the integral

$$\int\limits_0^1 \operatorname*{var}_{v\in\langle t,1\rangle} x(v)\,dt$$

has a finite value. Its value will be taken as the norm of the element x.

THEOREM 3. *For every function x, continuous in the interval $\langle 0,1\rangle$ and having a derivative at the point 0, the sequence*

$$\int_{\langle 0,1\rangle} x(t)\,dg_n(t) + a_n x(0) \qquad (g_n \in \Gamma)$$

tends to $x'(0)$ if, and only if, the following conditions are satisfied:

(1) *there exists a K such that*

$$\|g_n\| < K \quad \text{for} \quad n = 1,2,3,\ldots$$

(2) $\lim_{h\to 0+} g_n(h) = g_n(0+)$ *exists for* $n = 1,2,3,\ldots$ *and* $\lim_n (a_n - g_n(0+)) = 0$;

(3) $\lim_n \int_s^1 g_n(h)(2h-s)\,dh = 0$ *for any* $s \in \langle 0,1)$;

(4) $\lim_n \int_0^1 g_n(h)\,dh = -1$.

These theorems are proved by the methods of functional analysis. The proofs will appear in Studia Mathematica. Theorem 1 was obtained for the case $p=1$ by Fadeev [1] by the methods of real functions.

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MATHEMATICS

Some Conditions Sufficient for the Absolute Convergence of Multiple Fourier Series

by

J. MUSIELAK

Presented by W. ORLICZ on December 29, 1956

1. We shall consider real- or complex-valued functions $f(x_1,\dots,x_n)$ of n real arguments $x_1,\dots,x_n$, defined in the whole n-dimensional Euclidean space, periodic with period 2 in each variable, and integrable in the region $(0\leqslant x_i\leqslant 2;\ i=1,2,\dots,n)$ with the p-th power for a certain $1<p\leqslant 2$. Let $E=(1,2,\dots,n)$ be the set of all the numbers $1,2,\dots,n$. Let A be an arbitrary subset of the set E, and $\bar{A}$ the complement of A with regard to E. The numbers

$$a^A_{m_1,\dots,m_n}(f)=\int_0^{\pi}\dots\int f(x_1,\dots,x_n)\prod_{i\in A}\cos m_i\pi x_i\prod_{j\in\bar{A}}\sin m_j\pi x_j\,dx_1,\dots,dx_n$$

will be called the Fourier coefficients of the function $f(x_1,\dots,x_n)$ with respect to the trigonometrical system. Here, $A\subset E$; $m_1,\dots,m_n=0,1,2,\dots$, and $\prod_{i\in A}a_i$ denotes the product of all a_i with indices $i\in A$.

The series

$$(1.1)\qquad \sum_{m_1,\dots,m_n=0}^{\infty}\lambda_{m_1,\dots,m_n}\sum_{A\subset E}a^A_{m_1,\dots,m_n}(f)\prod_{i\in A}\cos m_i\pi x_i\prod_{j\in A}\sin m_j\pi x_j,$$

where

$$\lambda_{m_1,\dots,m_n}=2^{-\mu(H)},\qquad H=E\{m_\nu\neq 0\},$$

and where $\mu(H)$ is the number of all elements of the set H—is the Fourier series of the function $f(x_1,\dots,x_n)$. The sign $\sum_{A\subset E}$ indicates that the summation extends over all subsets A of the set E, including the empty subset.

Using this notation we shall present some conditions sufficient for convergence of the series

$$\sum_{m_1,\dots,m_n=0}^{\infty} (m_1+1)^{\beta_1}\dots(m_n+1)^{\beta_n}\varrho^{(\gamma)}_{m_1,\dots,m_n}(f), \tag{1.2}$$

where $\beta_1,\dots,\beta_n \geqslant 0$, $0<\gamma<2$ and

$$\varrho^{(\gamma)}_{m_1,\dots,m_n}(f)=\sum_{A\subset E}|a^A_{m_1,\dots,m_n}(f)|^{\gamma}.$$

It is clear that convergence of the series (1.2) with $\beta_1=\dots=\beta_n=0$ and $\gamma=1$ implies absolute convergence of the series (1.1).

2. We shall now introduce some necessary notations. Here, $H=(k_1,\dots,k_s)$ denotes a non-empty subset of the set E, where $k_1,\dots,k_s$ are the elements of H and $k_1<\dots<k_s$.

For $H=(k)$ we write

$$\Delta^H(f;\, x_1,\dots,x_n;\, h_1,\dots,h_n)=$$

$$=f(x_1,\dots,x_{k-1},\, x_k+h_k,\, x_{k+1},\dots,x_n)-f(x_1,\dots,x_{k-1},\, x_k,\, x_{k+1},\dots,x_n),$$

and for $H=(k_1,\dots,k_s)$ $(s>1)$

$$\Delta^H(f;\, x_1,\dots,x_n;\, h_1,\dots,h_n)=\Delta^{(k_s)}[\Delta^{H-(k_s)}(f);\, x_1,\dots,x_n;\, h_1,\dots,h_n].$$

We put

$$\omega^H(x_{l_1},\dots,x_{l_{n-s}};\, h_1,\dots,h_n)=\sup_{\substack{0\leqslant x_i\leqslant 2\\ |\delta_i|\leqslant h_i,\, i\in H}}|\Delta^H(f;\, x_1,\dots,x_n;\, \delta_1,\dots,\delta_n)|, \tag{2.1}$$

where $(l_1,\dots,l_{n-s})=\bar{H}$, and

$$\omega^H_p(h_1,\dots,h_n)=\Big[\sup_{\substack{|\delta_i|\leqslant h_i\\ i=1,\dots,n}}\int_0^2\int_0^2\dots\int_0^2|\Delta^H(f;\, x_1,\dots,x_n;\, \delta_1,\dots,\delta_n)|^p\, dx_1\dots dx_n\Big]^{1/p} \tag{2.2}$$

for $p>1$. The functions ω^H and ω^H_p will be called the modulus of continuity and the p-th integral modulus of the function $f(x_1,\dots,x_n)$, with regard to the set H, respectively.

We shall need the notion of the r-th variation $V^H_r(f)$ $(r\geqslant 1)$ of the function $f(x_1,\dots,x_n)$ with respect to the set $H\neq 0$ in the region $(0\leqslant x_i\leqslant 2;\ i=1,2,\dots,n)$. Let $H=(k_1,\dots,k_s)$ be non-empty, and let Π be the following partition of the n-dimensional parallelepiped $(0\leqslant x_i\leqslant 2;\ i=1,2,\dots,n)$ into partial n-dimensional parallelepipeds: $0=x_i^{(0)}<x_i^{(1)}\dots<x_i^{(N_i)}=2$; $i=1,2,\dots,n$.

We introduce

$$(2.3)\qquad V_r^H(f)=\Big[\sup_{0\leqslant x_i\leqslant 2}\sup_{\Pi}\sum_{i_{k_1}=1}^{N_{k_1}}\dots\sum_{i_{k_s}=1}^{N_{k_s}}|\Delta^H(f;\,x_1,\dots,x_{k_1-1},x_{k_1}^{(i_{k_1}-1)},$$

$$x_{k_1+1}\dots x_{k_s-1},x_{k_s}^{(i_{k_s}-1)},\,x_{k_s+1},\dots x_n;\,x_1^{(i_1)}-x_1^{(i_1-1)},\dots,x_n^{(i_n)}-x_n^{(i_n-1)})|^r\Big]^{1/r}.$$

$i\in\overline{H}$

3. With the above notations the following theorem holds.

THEOREM. *Let $\mathcal{H}$ be a class of non-empty subsets of the $E=(1,2,\dots,n)$ *). Let $f(x_1,\dots,x_n)$ be a periodic function with period 2 in each variable and integrable in the region $(0\leqslant x_i\leqslant 2;\ i=1,2,\dots,n)$ with the p-th power for a certain $1<p\leqslant 2$. We assume that for every $H\in\mathcal{H}$ there exists a number r_H satisfying the inequalities $1\leqslant r_H\leqslant p$, such that $V_{rH}^H(f)<\infty$. Further, we assume that for some $\beta_1,\dots,\beta_n\geqslant 0$ and $0<\gamma<2$ the following conditions are satisfied*

(*a*) *for $H=(k_1,\dots,k_s)\in\mathcal{H}$ we have*

$$(3.1)\qquad \omega^H(x_{l_1},\dots,x_{l_{n-s}};\,h_1,\dots h_n)\leqslant K_H(x_{l_1},\dots,x_{l_{n-s}})h_{k_1}^{\alpha_1^H}h_{k_2}^{\alpha_2^H}\dots h_{k_s}^{\alpha_s^H},$$

where $(l_1,\dots,l_{n-s})=\overline{H}$,

$$\int_0^2\int\dots\int[K_H(x_{l_1},\dots,x_{l_{n-s}})]^{p-r_H}\,dx_{l_1}\dots dx_{l_{n-s}}<\infty$$

and

$$\alpha_i^H>\frac{p(\beta_{k_i}+1-\gamma)}{\gamma(p-r_H)}\qquad \text{for}\qquad r_H\neq p,$$

$$\beta_{k_i}<\gamma-1\qquad \text{for}\qquad r_H=p;$$

(*b*) *for $H=(k_1,\dots,k_s)\in\mathcal{H}$ and $H\neq 0$ we have*

$$(3.2)\qquad \omega_p^H(h_1,\dots,h_n)\leqslant K_H h_{k_1}^{\alpha_1^H}h_{k_2}^{\alpha_2^H}\dots h_{k_s}^{\alpha_s^H},$$

where K_H is a constant and

$$\alpha_i^H>\frac{p(\beta_{k_i}+1-\gamma)+\gamma}{\gamma p}.$$

Under these conditions the series (1.2) *is convergent.*

To prove this theorem we use auxiliary functions defined as follows. For $H=(k)$

$$\mathcal{F}^H(f;\,x_1,\dots,x_n;\,h_1,\dots,h_n)=$$

$$=f(x_1,\dots,x_{k-1},x_k+h_k,x_{k+1},\dots,x_n)-f(x_1,\dots,x_{k-1},x_k-h_k,x_{k+1},\dots,x_n)$$

*) The class $\mathcal{H}$ may be empty.

and for $H=(k_1,\dots,k_s)$ $\quad(s>1,\ k_1<\dots<k_s)$

$$\mathcal{F}^H(f;\,x_1,\dots,x_n;\,h_1,\dots,h_n)=\mathcal{F}^{(k_s)}[\mathcal{F}^{H-(k_s)}(f);\,x_1,\dots,x_n;\,h_1,\dots,h_n].$$

The Fourier coefficients of the function $\mathcal{F}^H$ are

$$a^A_{m_1,\dots,m_n}(\mathcal{F}^H)=(-1)^{\mu(\bar{A}\cap H)}\,2^{\mu(H)}\prod_{i\in H}\sin m_i\pi h_i\,a^{A\Delta H}_{m_1,\dots,m_n}(f),$$

$\mu(B)$ being the number of all elements of the set B and $A\Delta H$ – the symmetric difference of the sets A and H. Applying the generalised Parseval formula to the function $\mathcal{F}^H$, suitable estimation leads to convergence of the series (1.2).

4. The above theorem is a generalisation of results obtained for two variables in papers [1] and [3]. The method of the proof given in our paper shows that a generalisation of Theorem III in [2] can be easily obtained. Moduli of the form (2.1) and (2.2) and conditions of the form (3.1) and (3.2) are used in the investigation on absolute convergence of double Fourier series in [1] and [2], and variations of the form (2.3) are applied in [2] and [3].

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MATHEMATICS

On the Uniform Convergences in Proximity Spaces

by

S. MRÓWKA

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The present paper introduces the notion of uniform convergence for sequences of functions, which take values from a proximity space. In our considerations the main role is played by a certain relation between sequences of elements of a proximity space (introduced by Efremovitch [1]) which, in the case of a metric proximity space, is equivalent to the relation $\varrho(x_n, y_n) \to 0$.

Definition 1. Let X be a proximity space and (x_n), (y_n) sequences of elements of this space. We shall write $x_n \sim y_n$ if for every increasing sequence (k_n) of positive integers the sets $\{x_{k_n}\}$ and $\{y_{k_n}\}$ are near.

The relation $\sim$ has the following properties:

THEOREM 1. *The relation $\sim$ is reflexive, symmetric and transitive.*

Proof. The reflexivity and the symmetry of the relation $\sim$ are obvious, only its transitivity requires a proof. Suppose $x_n \sim y_n$, $y_n \sim z_n$, and $x_n \nsim z_n$. There exists an increasing sequence (k_n) of positive integers such that the sets (x_{k_n}) and (z_{k_n}) are not near, hence there exist disjoint sets U_1 and U_2 such that $\{x_{k_n}\} \subset U_1$, $\{z_{k_n}\} \subset U_2$. Since $x_n \sim y_n$, $y_{k_n} \bar{\in} U_1$ for at most a finite number of n. Since $y_n \sim z_n$, $y_{k_n} \bar{\in} U_2$ for at most a finite number of n. It follows that there exists a point which belongs to $U_1 \cap U_2$, but this contradicts $U_1 \cap U_2 = 0$.

We shall note the following evident properties of the relation $\sim$:

1. If $x_n \sim y_n$, then for every increasing sequence (k_n) of positive integers $x_{k_n} \sim y_{k_n}$.

2. If $x_n \nsim y_n$, then there exists an increasing sequence (k_n) of positive integers such that for every subsequence (k_{l_n}) of the sequence (k_n) we have $x_{k_{l_n}} \nsim y_{k_{l_n}}$.

3. If $x_n \to x$, then $y_n \to x$ if, and only if, $x_n \sim y_n$.

4. If $x_n = y_n$ for almost all n, then $x_n \sim y_n$.

THEOREM 2. *If X is a metric proximity space then the relation $x_n \sim y_n$ is equivalent to the relation $\varrho(x_n, y_n) \to 0$.*

Proof. If $\varrho(x_n, y_n) \to 0$, then clearly $x_n \sim y_n$. Suppose $\varrho(x_n, y_n) \not\to 0$. It may be assumed that $\varrho(x_n, y_n) \geqslant \varepsilon > 0$. The following three cases are possible:

I there exists a finite system $\{x_1, \ldots, x_k\}$ of points such that

$$\min_{1 \leqslant i \leqslant k} \{\varrho(x_n, x_i)\} < \frac{\varepsilon}{4} \quad (n = 1, 2, \ldots);$$

II there exists a finite system $\{y_1, \ldots, y_s\}$ of points such that

$$\min_{1 \leqslant i \leqslant s} \{\varrho(y_n, y_i)\} < \frac{\varepsilon}{4} \quad (n = 1, 2, \ldots);$$

III there exists an increasing sequence (r_n) of positive integers such that

$$\varrho(x_{r_n}, x_{r_m}) \geqslant \frac{\varepsilon}{4}, \quad \varrho(y_{r_n}, y_{r_m}) \geqslant \frac{\varepsilon}{4} \quad \text{for} \quad n, m = 1, 2, \ldots; n \neq m,$$

In the first case there exists a point x_{i_0} and an increasing sequence (p_n) of positive integers such that $\varrho(x_{p_n}, x_{i_0}) < \varepsilon/4$. But $\varrho(y_{p_m}, x_{p_n}) \geqslant \varrho(y_{p_m}, x_{p_m}) - \varrho(x_{p_m}, x_{p_n})$ and $\varrho(x_{p_n}, x_{p_m}) < \varepsilon/2$; thus $\varrho(x_{p_n}, x_{p_m}) \geqslant \varepsilon - \varepsilon/2 = \varepsilon/2$, whence the sets (x_{p_n}) and (y_{p_n}) are not near. In the second case the pattern of proof is similar. In the third case the proof is as follows: let $k_1 = 1$ and suppose that there are defined numbers $k_1 < k_2 < \ldots < k_{n_0}$ such that $\varrho(x_{k_i}, y_{k_j}) \geqslant \varepsilon/8$ for $i, j \geqslant n_0$. There is at most a finite number of points $x \in \{x_n\}_{n < k_{n_0}}$ such that the distance between x_n and the set $\{x_{k_i}\} \cup \{y_{k_i}\}$ $(i \leqslant n_0)$ is less than $\varepsilon/8$ and the same holds true for the set $\{y_n\}_{n \geqslant k_{n_0}}$ Thus there exists a number $n' > k_{n_0}$ such that the distances between the points $x_{n'}, y_{n'}$ and the set $\{x_{k_i}\} \cup \{y_{k_i}\}$ $(i \leqslant n_0)$ are greater than $\varepsilon/8$. Let $k_{n_0+1} = n'$. Thus for the obtained sequence (k_n), the sets $\{x_{k_n}\}$ and $\{y_{k_n}\}$ are not near.

A sequence (x_n) of elements of a proximity space is said to be *fundamental*, if $x_n \sim x_{k_n}$ for every increasing sequence (k_n) of positive integers. From 3. it follows immediately that every convergent sequence is fundamental and from Theorem 2 it follows that, in the case of a metric proximity space, this definition agrees with the ordinary "metric" definition and that a metric proximity space is complete if, and only if, every fundamental sequence of its elements is convergent. It implies the following theorem, due to Smirnov [2]:

THEOREM 3. *Let X be a complete metric proximity space and uX its compactification. Then the first axiom of countability is not fulfilled at any point of $uX \setminus X$.*

Proof. If the first axiom of countability is fulfilled at a point $x \in uX$, then there exists a sequence of elements of X which converges

to x. This sequence is fundamental and by the completeness of X it converges to a point of X, hence $x \in X$.

Definition 2. Let Y be a proximity space and X an arbitrary set and let $f_n \in Y^X$ $(n=1,2,\ldots)$. The sequence (f_n) is said to be uniformly convergent to $f \in Y^X$ (in symbols $f_n \Rightarrow f$) in $f_n(x_n) \sim f(x_n)$ for every sequence (x_n) of elements of X.

From Theorem 2 immediately follows that in the case of a metric proximity space the definition agrees with that commonly used. It may be easily proved that

5. The space Y^X with the uniform convergence is an $\mathcal{L}^*$-space.

6. If $f_n \Rightarrow f$, then $f_n(x) \to f(x)$ for every $x \in X$.

THEOREM 4. *If X is a topological space and f_n are sequentially continuous at a point $x_0 \in X$ $(n=1,2,\ldots)$ and $f_n \Rightarrow f$, then f is also sequentially continuous at the point x_0.*

Proof. Suppose $x_n \to x_0$ and $f(x_n) \not\to f(x_0)$. One may assume that there exists a neighbourhood U of the point $f(x_0)$ such that $f(x_n) \overline{\in} U$ for every n. Then there exists a neighbourhood U_1 of $f(x_0)$ such that $U_1 \Subset U$. Since $f_n(x_0) \to f(x_0)$ and f_n are sequentially continuous at x_0, for every n a number k_n may be found such that $f_n(x_{k_n}) \in U_1$, whence $f_n(x_{k_n}) \not\sim f(x_{k_n})$ and the theorem follows.

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MATHEMATICS

On the Representation of Quasi-Boolean Algebras

by

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Presented by A. MOSTOWSKI on January 5, 1957

The researches on the algebraic treatment of constructive logic with strong negation *), which will be discussed in a separate paper, suggest the examination of a certain kind of lattices here called quasi-Boolean algebras. The aim of this paper is to give the representation theorem of these lattices.

We shall say that an abstract algebra $\langle A, +, \cdot, \sim\rangle$ is a *quasi-Boolean algebra* when:

(i) $\langle A, +, \cdot\rangle$ is a distributive lattice with the zero element 0 and the unit element 1,

(ii) $\sim$ is a unary operation which satisfies the following conditions:

$$\sim\sim a = a, \qquad \sim(a \cdot b) = \sim a + \sim b \quad \text{for any} \quad a, b \in A.$$

The operation $\sim$ will be called the *quasi-complement*.

1) *In any quasi-Boolean algebra* $\langle A, +, \cdot, \sim\rangle$

$$\sim(a+b) = \sim a \cdot \sim b \quad \textit{for any} \quad a, b \in A,$$

$$\sim 0 = 1, \qquad \sim 1 = 0.$$

This is an immediate consequence of the definition.

Let $\mathfrak{X}$ be a non-empty set and let g be a one-to-one mapping of $\mathfrak{X}$ onto $\mathfrak{X}$ which is an involution, i. e.,

$$g(g(x)) = x \quad \text{for every} \quad x \in \mathfrak{X}.$$

Setting $\sim X = \mathfrak{X} - g(X)$ for every $X \subset \mathfrak{X}$ we find that every family of subsets of the set $\mathfrak{X}$, which is closed under this operation as well under the set-theoretical operations of sum and product, is a quasi-Boolean algebra. Every quasi-Boolean algebra of this kind is said to be a *quasi-*

*) For constructive logic with strong negation cf. [1], [2] and [3].

-field of sets. We shall prove that every quasi-Boolean algebra is isomorphic with a quasi-field of sets, using the method of Stone [4].

Let $\langle A, +, \cdot, \sim\rangle$ be an arbitrary but fixed quasi-Boolean algebra. A non-void subset $\mathfrak{i} \subset A$ is said to be an *ideal* (a *filter*), when $\mathfrak{i} \neq A$ and

(i) if $a, b \in \mathfrak{i}$, then $a+b \in \mathfrak{i}$ $(a \cdot b \in \mathfrak{i})$,

(ii) if $a \in \mathfrak{i}$ and $b \in A$, then $a \cdot b \in \mathfrak{i}$ $(a+b \in \mathfrak{i})$.

An *ideal* $\mathfrak{p}$ (a *filter* $\mathfrak{q}$) is said to be *prime* provided that if $a \cdot b \in \mathfrak{p}$ $(a+b \in \mathfrak{q})$, then either $a \in \mathfrak{p}$ or $b \in \mathfrak{p}$ (either $a \in \mathfrak{q}$ or $b \in \mathfrak{q}$).

Given a subset $A_0 \subset A$, let $\widetilde{A}_0$ be the set of all elements $\sim x$ such that $x \in A_0$. It is easy to see that

2) *If* $\mathfrak{q}$ *is a filter, then* $\widetilde{\mathfrak{q}}$ *is an ideal. Moreover, if* $\mathfrak{q}$ *is a prime filter, then* $\widetilde{\mathfrak{q}}$ *is a prime ideal.*

It is known that

3) *If* $\mathfrak{p}$ *is a prime ideal, then* $A - \mathfrak{p}$ *is a prime filter.*

Let $\mathfrak{X}$ be the set of all prime filters of the quasi-Boolean algebra $\langle A, +, \cdot, \sim\rangle$. For every $\mathfrak{q} \in \mathfrak{X}$ let

$$(*) \qquad g(\mathfrak{q}) = A - \widetilde{\mathfrak{q}}.$$

It follows from the definition of the mapping g and from 2) and 3) that g is a one-to-one mapping of $\mathfrak{X}$ onto $\mathfrak{X}$. Moreover,

$$g(g(\mathfrak{q})) = \mathfrak{q} \quad \text{for every} \quad \mathfrak{q} \in \mathfrak{X}.$$

For every $a \in A$, let $h(a)$ be the class of all prime filters $\mathfrak{q}$ such that $a \in \mathfrak{q}$.

4) *The mapping* h *is an isomorphism of* A *into the quasi-field of all subsets of* $\mathfrak{X}$, *the operation* $\sim$ *being defined as follows*:

$$\sim X = \mathfrak{X} - g(X) \quad \textit{for every} \quad X \subset \mathfrak{X}.$$

Indeed, it is known from [4] that h is an isomorphism of the distributive lattice $\langle A, +, \cdot\rangle$ into the ring of *all* subsets of $\mathfrak{X}$. To prove 4) it suffices to show that

$$(**) \qquad h(\sim a) = \sim h(a), \quad \text{for every} \quad a \in A.$$

To prove (**) let us notice that on account of (*) the condition $\mathfrak{q} \in g(h(a))$ is equivalent to the existence of a prime filter $\mathfrak{q}_1$, belonging to $h(a)$ such that $\mathfrak{q} = g(\mathfrak{q}_1)$, i. e., $\mathfrak{q} = A - \widetilde{\mathfrak{q}}_1$. On account of the equivalences

$$\mathfrak{q}_1 \in h(a) \equiv a \in \mathfrak{q}_1 \equiv \sim a \in \widetilde{\mathfrak{q}}_1 \equiv \sim a \notin A - \widetilde{\mathfrak{q}}_1$$

we obtain that $\mathfrak{q} \in g(h(a))$ if, and only if, there exists a prime filter $\mathfrak{q}_1$ such that $\mathfrak{q} = g(\mathfrak{q}_1)$ and $\sim a \notin \mathfrak{q}$. Since the mapping g transforms $\mathfrak{X}$ onto $\mathfrak{X}$ we infer that for every $\mathfrak{q} \in \mathfrak{X}$ there exists a $\mathfrak{q}_1 \in \mathfrak{X}$ such that

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$\mathfrak{q} = g(\mathfrak{q}_1)$. In consequence, $\mathfrak{q} \in g(h(a))$ if, and only if, $\sim a \notin \mathfrak{q}$. Hence $\mathfrak{q} \in \sim h(a)$ if, and only if, $\mathfrak{q} \in h(\sim a)$; which completes the proof of 4).

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THEORETICAL PHYSICS

An Approximation for the Physical Nucleon in the Fixed-Source Theory

by

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In this paper *) an approximation procedure is given for solving the model of the physical nucleon, which was proposed in the preceding notes [1], [2].

So far I have not managed to solve the Equation (2.12) exactly. Formally, it represents the problem of nine oscillators in the 3-space interacting by means of the potential $V_\alpha(q)$. The solution is given here after an approximation procedure is assumed.

Let us remark that the operators σ_i and τ_j appear symmetrically in the Hamiltonian $H^{\text{int}}(q) = -\bar{g}\sigma_i\tau_j q_{ij}$. Our approximation procedure will depend on the assumption that in the four ground states α of the physical nucleon only these values of the co-ordinates q_{ij} are of importance for which $q_{ij} \approx q_{ji}$. Using this assumption we shall try to estimate the masses of the ground states of the four isobars and to seek a connection of our results with experimental data.

We write

$$q_{ij} = Q_{ij} + r_{ij}, \quad \text{where} \quad Q_{ij} = \tfrac{1}{2}(q_{ij} + q_{ji}) \quad \text{and} \quad r_{ij} = \tfrac{1}{2}(q_{ij} - q_{ji})$$

are the symmetrical and antisymmetrical parts of q_{ij} respectively. Denoting by P_{ij} and s_{ij} the canonical momenta conjugated with Q_{ij} and r_{ij} respectively

$$[P_{ij}, Q_{kl}] = -i\hbar\delta_{ik}\delta_{jl}, \quad [s_{ij}, r_{kl}] = -i\hbar\delta_{ik}\delta_{jl} \quad (i \neq j,\ k \neq l)$$

($r_{ll} = 0$, $s_{ii} = 0$), we have

$$P_{ij} = \begin{cases} P_{ij} & i = j \\ \frac{1}{2}(P_{ij} + s_{ij}) & i \neq j \end{cases}.$$

*) This paper is the sequel of papers [1] and [2].

Thus,

$$\tfrac{1}{2}(p_{ij}^2+\omega^2 q_{ij}^2)=\sum_i \tfrac{1}{2}(P_{ii}^2+\omega^2 Q_{ii}^2)+\sum_{i\neq j}\tfrac{1}{8}[P_{ij}^2+(2\omega)^2 Q_{ij}^2]+\sum_{i\neq j}[s_{ij}^2+(2\omega)^2 r_{ij}^2].$$

Now we represent the interaction Hamiltonian as follows

$$H^{\mathrm{int}}(q)=H^{\mathrm{int}}(Q)-\bar{g}\sigma_i\tau_j r_{ij}=H_1^{\mathrm{int}}(Q)+H_2^{\mathrm{int}}(Q)-\bar{g}\sigma_i\tau_j r_{ij},$$

where

$$H_1^{\mathrm{int}}(Q)=\sigma_i\tau_i \underline{u}_i(Q),$$

$$H_2^{\mathrm{int}}(Q)=(U\sigma_i\tau_i U^{-1}-\sigma_i\tau_i)\underline{u}_i(Q),$$

and U depends on Q and in general on $\vec{\sigma}$ and $\vec{\tau}$. The part $H_1^{\mathrm{int}}(Q)$ gives the "potentials"

$$V_\alpha(Q)=e_i^{(\alpha)}\underline{u}_i(Q) \qquad (\alpha=1,2,3,4).$$

As unperturbed Hamiltonian we shall treat now the operator

$$\overset{0}{H}=\sum_{i\neq 1}H_i^M(\varphi,\pi)+\sum_{n>1}\tfrac{1}{2}(p_{ijn}^2+\omega_{nn}^2 q_{ijn}^2)+\sum_{n>n'>1}\omega_{nn'}^2 q_{iju}q_{ijn'}+$$

$$+\tfrac{1}{2}(p_{ij}^2+\omega^2 q_{ij}^2)+H_1^{\mathrm{int}}(Q),$$

and as the perturbation of $\overset{0}{H}$ the Hamiltonian

$$\overset{1}{H}=\sum_{n>1}\omega_{n1}^2(q_{ijn}Q_{ij}+q_{ijn}r_{ij})+H_2^{\mathrm{int}}(Q)-\bar{g}\sigma_i\tau_j r_{ij}.$$

Transitions between different sets α are now caused by the operator $H_2^{\mathrm{int}}(Q)-\bar{g}\sigma_i\tau_j r_{ij}$. Probabilities of these transitions are given by products of this operator and the operator $\sum_{n>1}\omega_{n1}^2(q_{ijn}Q_{ij}+q_{ijn}r_{ij})$. The latter operator causes, on the other hand, also transitions inside the same set α of states. Transitions between different α's appear in our approximation procedure (just as in the preceding paper), in the second order, whereas transitions within the same α appear already in the first order.

If $Q=(Q_{ij})$ is a symmetrical matrix, we may transform it into the diagonal form $Q=(Q_i\delta_{ij})=AQA^T$ (in the general case one may diagonalise only the symmetrical matrix qq^T and obtain in this way formulae (1.15), (1.6), (1.7), (1.8), where $u_{ij}(\varphi)=-\bar{g}q_{ij}$).

We thus obtain four "potentials" $V_\alpha(\varphi)=V_\alpha(Q)$ $(\alpha=1,2,3,4)$ given by (1.15), where now $\underline{u}_i(\varphi)=\underline{u}_i(Q)=-\bar{g}Q_i$ $(i=1,2,3)$ are the roots of the secular equation

$$-\underline{u}_i^3+S(\varphi)\underline{u}_i^2-M(\varphi)\underline{u}_i+D(\varphi)=0 \tag{3.1}$$

(instead of (1.6)) in which now (not to be confounded with (1.7)),

$$(3.2)\qquad \begin{cases} S'(\varphi)=\operatorname{sp} u=\sum_{i=1}^{3} u_{ii}, \\ D(\varphi)=\det u, \\ M(\varphi)=\sum_{i=1}^{3} [\text{minor of } D \text{ corresponding to } u_{ii}] \end{cases}$$

$(u_{ij}(\varphi)=-\bar{g}Q_{ij})$.

We have, of course,

$$(3.3)\qquad \begin{cases} S(\varphi)=\sum_{i=1}^{3} \underline{u}_i, \\ D(\varphi)=\underline{u}_1\underline{u}_2\underline{u}_3, \\ M(\varphi)=\underline{u}_2\underline{u}_3+\underline{u}_3\underline{u}_1+\underline{u}_1\underline{u}_2 \end{cases}$$

$(u_i(\varphi)=-\bar{g}Q_i(Q))$.

If $Q=(Q_{ij})$ is symmetrical, we have

$$\sigma_i'=A_{ij}\sigma_j=U\sigma_iU^{-1}, \qquad \tau_i'=A_{ij}\tau_j=U\tau_iU^{-1},$$

where

$$U=e^{i(\sigma_3+\tau_3)c/2}e^{i(\sigma_2+\tau_2)a/2}e^{i(\sigma_3+\tau_3)b/2},$$

if we represent the $A=(A_{ij})$ by means of three Euler angles a,b,c (cf. [3]):

$$A=\begin{pmatrix} \cos a\cos b\cos c-\sin b\sin c, & -\cos a\cos b\sin c-\sin b\cos c, & \sin a\cos b \\ \cos a\sin b\cos c+\cos b\sin c, & -\cos a\sin b\sin c+\cos b\cos c, & \sin a\sin b \\ -\sin a\cos b, & \sin a\, a\sin b, & \cos a \end{pmatrix}.$$

Here, the angles a,b,c and also A and U depend on φ or rather on Q.

We note that for $\alpha=1$ we have $U|\alpha>^s=|\alpha>^s$, because for $\alpha=1$, $(\vec{\sigma}+\vec{\tau})|\alpha>^s=0$ (see (1.12), (1.13) and (1.15)), and thus for $\alpha=1$ we obtain $H_2^{\text{int}}(Q)|\alpha>^s=0$. Thus,

$$^s<\alpha|H_2^{\text{int}}(Q)|\alpha'>^s=0, \qquad \text{if} \quad \alpha=1 \quad \text{or} \quad \alpha'=1,$$

and then only the operator $-\bar{g}\sigma_i\tau_jr_{ij}$ gives contributions to matrix elements of $H_2^{\text{int}}(Q)-\bar{g}\sigma_i\tau_jr_{ij}$.

It follows from (1.15), (3.3) and (3.2) that for $\alpha=1$

$$(3.4)\qquad V_1(Q)=\bar{g}(Q_{11}+Q_{22}+Q_{33})=\bar{g}(q_{11}+q_{22}+q_{33})$$

$(Q_{ii}=q_{ii})$.

Performing the unitary transformation given by the operator $\exp(i\lambda\sum_i p_{ii})$ $(P_{ii}=p_{ii})$, where λ is a c-number, we have

$$e^{\frac{i\lambda\Sigma p_{ii}}{i}}\Big[\tfrac{1}{2}(p_{ij}^2+\omega^2 q_{ij}^2)+\bar{g}\sum_i q_{ii}\Big]e^{-\frac{i\lambda\Sigma p_{ii}}{i}}=$$

$$(3.5)\qquad =\tfrac{1}{2}(p_{ij}^2+\omega^2 q_{ij}^2)+\bar{g}\sum_i q_{ii}+\lambda\hbar\Big(\omega^2\sum_i q_{ii}+3\bar{g}\Big)+3\lambda^2\frac{\hbar^2}{2}\omega^2=$$

$$=\tfrac{1}{2}(p_{ij}^2+\omega^2 q_{ij}^2)-\tfrac{2}{3}\frac{\bar{g}^2}{\omega^2},$$

if we put $\lambda=-\bar{g}/\hbar\omega^2$. The eigenvalues of the Hamiltonian $\frac{1}{2}(p_{ij}^2+\omega^2 q_{ij}^2)+V_1(Q)$, appearing in Equation (2.12) after the part $-\bar{g}\sigma_i\tau_j r_{ij}$ is removed to the interaction, have therefore the form

$$(3.6)\qquad E_{1,A}=E_{1,N_{i1}}=\sum_{ij}(N_{ij}+\tfrac{1}{2})\hbar\omega-\tfrac{3}{2}\frac{\bar{g}^2}{\omega^2}=\sum_{ij}N_{ij}\hbar\omega+\tfrac{9}{2}\hbar\omega-\tfrac{3}{2}\frac{\bar{g}^2}{\omega^2},$$

where $N_{ij}=N_{ji}$ are integers. $\frac{9}{2}\hbar\omega$ is due of course, to zero point energy. These eigenvalues represent in our approximation the energy levels of the isobar $\alpha=1$ of the physical nucleon. The ground level $(N_{1,1}=0)$ of this isobar has energy $E_{1,0}=\frac{9}{2}\hbar\omega-\frac{3}{2}\bar{g}^2/\omega^2$ (or rather $Mc^2+E_{1,0}$). It corresponds to the experimental mass $M_1=M+\frac{9}{2}\hbar\omega/c^2-\frac{3}{2}\bar{g}^2/\omega^2c^2$.

"Potentials" $V_\alpha(Q)$ other than $V_1(Q)$ may be written according to (1.15) in the forms

$$(3.7)\qquad \begin{cases} V_2(Q)=-V_1(Q)-2\underline{u}_1(Q)=-V_1(Q)+2\bar{g}\underline{Q}_1(Q), \\ V_3(Q)=-V_1(Q)-2\underline{u}_2(Q)=-V_1(Q)+2\bar{g}\underline{Q}_2(Q), \\ V_4(Q)=-V_1(Q)-2\underline{u}_3(Q)=-V_1(Q)+2\bar{g}\underline{Q}_3(Q). \end{cases}$$

We note that, by virtue of (3.4), $V_1(Q)=-V_1(-Q)$ and the equations

$$(3.8)\qquad [\tfrac{1}{2}(p_{ij}^2+\omega^2 q_{ij}^2)\mp V_1(Q)+2\bar{g}\underline{Q}_{\alpha-1}(Q)]\Phi_{\alpha A}(\pm q)=E_{\alpha A}\Phi(\pm q)$$
$$(\alpha=2,3,4)$$

have by pairs the same eigenvalues. The terms $2\bar{g}\underline{Q}_i(-Q)$ $(i=1,2,3)$ describe the mass differences between the isobars $\alpha=2,3,4$ and the isobar $\alpha=1$. Thus, if we admitted the supposition that the masses of four ground states of the sets $\alpha=1,2,3,4$ correspond to those of the four barions N, Λ, Σ, Ξ, the order of magnitude of terms $2g\underline{Q}_i(-Q)$ should be equal to 10-30 per cent of M_1c^2 (M_1—the experimental mass of the isobar $\alpha=1$). One may then try to consider the terms $2\bar{g}\underline{Q}_i(-Q)$ as perturbation of the operator $Mc^2+\frac{1}{2}(p_{ij}^2+\omega^2 q_{ij}^2)+V_1(Q)$, the ground level of which has energy M_1c^2.

Using the first order perturbation method we obtain

$$(3.9)\qquad M_\alpha-M_1=\frac{2\bar{g}}{c^2}\int dq\Phi_{1,0}^*(q)\underline{Q}_{\alpha-1}(-Q)\Phi_{1,0}(q)=$$

$$=\frac{2\bar{g}}{c^2}\int dQ\Phi_{1,0}^{(1)*}(Q)\underline{Q}_{\alpha-1}(-Q)\Phi_{1,0}^{(1)}(Q)\qquad(\alpha=2,3,4),$$

where

$$dq = 2^3 dQ\, dr,\quad dQ = dQ_{11} dQ_{22} dQ_{33} dQ_{12} dQ_{13} dQ_{23},\quad dr = dr_{12} dr_{13} dr_{23}$$

and

$$[Mc^2 + \tfrac{1}{2}(p_{ij}^2 + \omega^2 q_{ij}^2) + V_1(Q)]\Phi_{1,0}(q) = M_1 c^2 \Phi_{1,0}(q)$$

($M_1 c^2 = Mc^2 + E_{1,0}$). The eigenfunction $\Phi_{1,0}(q)$ has the form

$$\Phi_{1,0}(q) = e^{-i\lambda \sum_i p_{ii}} \left(\frac{\omega}{\pi\hbar}\right)^{9/4} e^{-\frac{1}{2}\frac{\omega}{\hbar}\sum_{ij} q_{ij}^2} = \tag{3.10}$$

$$= \left(\frac{\omega}{\pi\hbar}\right)^{9/4} e^{-\frac{1}{2}\frac{\omega}{\hbar}\left[\sum_i (q_{ii} - \hbar\lambda)^2 + \sum_{i\neq j} q_{ij}^2\right]} = \frac{1}{2^3}\Phi_{1,0}^{(1)}(Q)\Phi_{1,0}^{(2)}(r),$$

where

$$\Phi_{1,0}^{(1)}(Q) = 2^{3/2}\left(\frac{\omega}{\pi\hbar}\right)^{3/2} e^{-\frac{1}{2}\frac{\omega}{\hbar}\left[\sum_i (Q_{ii} - \hbar\lambda)^2 + \sum_{i\neq j} Q_{ij}^2\right]},$$

$$\Phi_{1,0}^{(2)}(r) = 2^{3/2}\left(\frac{\omega}{\pi\hbar}\right)^{3/4} e^{-\frac{1}{2}\frac{\omega}{\hbar}\sum_{i\neq j} r_{ij}^2},$$

and $\lambda = \bar{g}/\hbar\omega^2$ (see (3.5)).

We note that from (3.9) and (3.10) it follows

$$\sum_{a=2}^{4} M_a - 3M_1 = \frac{2\bar{g}}{c^2}\int dQ\, \Phi_{1,0}^{(1)*} \sum_i \underline{Q}_i(-Q)\Phi_{1,0}^{(1)}(Q) =$$

$$= -\frac{2\bar{g}}{c^2}\int dq\, \Phi_{1,0}^{(1)*}(Q) S(-Q)\Phi_{1,0}^{(1)}(Q) = \tag{3.11}$$

$$= -\frac{2\bar{g}}{c^2}\, dq\, \Phi_{1,0}^{(1)} \sum_i Q_{ii}\Phi_{1,0}^{(1)}(Q) = -\frac{6\bar{g}}{c^2}\hbar\lambda = \frac{6\bar{g}^2}{\omega^2 c^2}.$$

By virtue of (3.1) we obtain

$$\begin{cases} \underline{u}_1(Q) = -\bar{g}\underline{Q}_1(Q) = \frac{1}{3}S(Q) + a(Q) + b(Q), \\ \underline{u}_2(Q) = -\bar{g}\underline{Q}_2(Q) = \frac{1}{3}S(Q) + \varepsilon a(Q) + \varepsilon^2 b(Q), \\ \underline{u}_3(Q) = -\bar{g}Q_2(Q) = \frac{1}{3}S(Q) + \varepsilon^2 a(Q) + \varepsilon b(Q), \end{cases} \tag{3.12}$$

where

$$\begin{cases} a(Q) = \left\{-\frac{s}{2} + \left[\left(\frac{s}{2}\right)^2 + \left(\frac{r}{3}\right)^3\right]^{1/2}\right\}^{1/3}, \\ b(Q) = \left\{-\frac{s}{2} - \left[\left(\frac{s}{2}\right)^2 + \left(\frac{r}{3}\right)^3\right]^{1/2}\right\}^{1/3} = a^*(Q), \\ r(Q) = M - \frac{1}{3}S^2, \qquad s(Q) = -D + \frac{1}{3}SM - \frac{2}{27}S^3, \end{cases} \tag{3.13}$$

($b = a^*$ since the Equation (3.1) has real roots, because the matrix $Q = (Q_{ij})$ is symmetrical) and $\varepsilon = (-1 - \sqrt{-3})/2$, $\varepsilon^2 = -(1 + \sqrt{3})/2$. $S(Q)$, $D(Q)$, $M(Q)$, are given by (3.2).

Inserting (3.12) in (3.9) and using (3.11) we obtain

$$\begin{cases} M_2 = M_1 + \dfrac{2\bar{g}^2}{\omega^2 c^2} - 2\,\mathrm{Re}\,A, \\ M_3 = M_1 + \dfrac{2\bar{g}^2}{\omega^2 c^2} + \mathrm{Re}\,A - \sqrt{3}\,\mathrm{Im}A, \\ M_4 = M_1 + \dfrac{2\bar{g}^2}{\omega^2 c^2} + \mathrm{Re}\,A + \sqrt{3}\mathrm{Im}\,A, \end{cases} \tag{3.14}$$

where

$$A = \frac{2}{c^2}\int dQ\,\Phi^{(1)*}_{1,0}(Q)\,a(-Q)\,\Phi^{(1)}_{1,0}(Q). \tag{3.15}$$

It follows from (3.14) that

$$\begin{cases} M_2 - M_1 = \dfrac{2\bar{g}}{\omega^2 c^2} - 2\,\mathrm{Re}\,A, \\ M_3 - M_2 = 3\,\mathrm{Re}\,A - \sqrt{3}\,\mathrm{Im}\,A, \\ M_4 - M_3 = 2\sqrt{3}\mathrm{Im}\,A. \end{cases} \tag{3.16}$$

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An Estimate of Masses of Isobars of the Nucleon in the Fixed-Source Theory

by

W. KRÓLIKOWSKI

Presented by W. RUBINOWICZ on October 29, 1956

In this paper*) an estimate of the masses of four isobars is carried out. It is possible to achieve a satisfactory agreement between the masses of four isobars in this model and the masses of four known types of barions (N, Λ, Σ, Ξ). But the isotopic spin properties of the isobars (see (1.12) and (1.13)) are different in this case from those which are probably the properties of the barions.

We may rewrite the integral (3.15) by virtue of (3.10) in the form

$$A=\frac{2}{c^2}\int dQ\Phi^{(1)2}_{1,0}(Q)a(-Q)=\frac{2}{c^2}\int dQ[e^{-i\lambda\Sigma P_{ii}}f(Q)]a(-Q)=$$

$$=\frac{2}{c^2}\int dQf(Q)e^{i\lambda\Sigma P_{ii}}a(-Q)=\frac{2}{c^2}\int dQf(Q)a(-Q_{ij}-\hbar\lambda\delta_{ij}),$$

where

$$f(Q)=2^3\left(\frac{\omega}{\pi\hbar}\right)^3 e^{-\frac{\omega}{\hbar}\Sigma Q^2_{ij}}.$$

Using the estimate

$$\int_{-\infty}^{+\infty}(6)\int dQf(Q)(\ldots)\approx\frac{1}{2^6}\left(\frac{\omega}{\hbar}\right)^3\int_{-(\hbar/\omega)^{1/2}}^{+(\hbar/\omega)^{1/2}}(6)\int dQ(\ldots)$$

we obtain

$$A\approx\frac{2}{c^2}\frac{1}{2^6}\left(\frac{\omega}{\hbar}\right)^{1/2}\int_{-(\hbar/\omega)^{1/2}}^{+(\hbar/\omega)^{1/2}}(6)\int dQa(-Q_{ij}-\hbar\lambda\delta_{ij})= \tag{4.1}$$

$$=\frac{2g^{-2}}{\omega^2c^2}\frac{(\hbar\omega)^{1/2}}{\bar{g}/\omega}\frac{1}{2^6}\int_{-1}^{+1}(6)\int d\xi a'\left(-\xi_{ij}+\frac{\bar{g}/\omega}{(\hbar\omega)^{1/2}}\delta_{ij}\right),$$

*) This paper is the sequel of *An Approximation for the Physical Nucleon in the Fixed Source Theory* (in this issue) and of two papers published in a previous issue [1], [2].

where $Q_{ij}=(\hbar/\omega)^{1/2}\xi_{ij}$, $a(Q)=\bar{g}a'(Q)$ (and $\lambda=-\bar{g}\hbar/\omega^2$). Above we made use of the fact that $a(Q)=(\hbar/\omega)^{1/2}a(\xi)$, as follows from (3.13) and (3.2).

We put $M_2+M_3+M_4=M_\Lambda+M_\Sigma+M_\Xi$, where M_Λ, M_Σ, M_Ξ are the experimental masses of the barions Λ, Σ, Ξ. Then by (3.11) we obtain

$$\frac{2\bar{g}^2}{\omega^2c^2}=\frac{1}{3}\sum_{\beta=2}^{4}(M_\beta-M_1)=\frac{1}{3}(M_\Lambda+M_\Sigma+M_\Xi)-M_N=526\ m_e, \tag{4.2}$$

where we have anticipated the fact that $M_1=M_N=1836\ m_e$ is the mass of the physical nucleon (N), the relation (4.2) determining the value of the constant $\bar{g}/\omega$. It turns out, now, that it is possible to choose the value of the second constant in the integral (4.1), $(\bar{g}/\omega)(\hbar\omega)^{1/2}$ so that a satisfactory agreement between M_2, M_3, M_4 and three experimental masses M_Λ, M_Σ, M_Ξ is achieved.

A crude numerical calculation of the integral (4.1), using the Tchebyshev approximation (with two points for each of six dimensions, i. e. together 2^6 points) was carried out for several values of $(\bar{g}/\omega)(\hbar\omega)^{1/2}$. Then the formula (3.14) was used. The comparison of results with the experimental masses of barions Λ, Σ, Ξ is shown as follows:

			$\sqrt{3}$		$2=\sqrt{4}$		$\frac{4}{\sqrt{3}}=\sqrt{5\frac{1}{3}}\approx\sqrt{5}$		$\frac{5}{\sqrt{3}}=\sqrt{8\frac{1}{3}}\approx\sqrt{8}$	
	M_{exp}	a	M	Δ	M	Δ	M	Δ	M	Δ
Λ	2190	2	2033	−157	2084	−106	2132	− 58	2162	−28
Σ	2325	3	2362	+ 37	2345	+ 20	2278	− 47	2362	+37
Ξ	2570	4	2691	+121	2658	+ 88	2675	+105	2561	− 9

where $\Delta=M-M_{\text{exp}}$, and $(\bar{g}/\omega)(\hbar\omega)^{1/2}=\sqrt{3}$, $\sqrt{4}$, $\sqrt{5\frac{1}{3}}$, $\sqrt{8\frac{1}{3}}$.

Thus, using our approximation procedure, the rough perturbation method (3.9) and the crude approximation of the integral (3.15) we get a tentative correspondence between the masses of our four isobars and of known barions.

The constants

$$\bar{g}^2=\frac{4\pi}{c}C, \qquad \omega^2=\frac{1}{C}\int_0^\infty r^2dr\frac{d\varrho}{dr}c^2\left(-\frac{d^2}{dr^2}-\frac{2}{r}\frac{d}{dr}+\frac{2}{r^2}+\mu^2\right)\frac{d\varrho}{dr} \tag{4.3}$$

(where $C=\int_0^\infty r^2dr(d\varrho/dr)^2$) appearing in our treatment depend on the constant of pseudoscalar coupling g and on the shape of the source $\varrho(r)$. Taking into account, e. g. the Gaussian distribution,

$$\varrho = \sqrt{\frac{2}{\pi}} \frac{1}{r_0^3} e^{-1/2(r/r_0)^2} \quad \left(\int d_3x \varrho = 4\pi \int_0^\infty r^2 dr \varrho = 1 \right), \tag{4.4}$$

we have

$$C = \int_0^\infty r^2 dr \left(\frac{d\varrho}{dr} \right)^2 = 3 \sqrt{\frac{2}{\pi}} \frac{1}{r_0^5}$$

and for the shape of the meson cloud

$$u_1(r) = \frac{1}{C^{1/2}} \frac{d\varrho}{dr} = -\frac{1}{\sqrt{3}} \sqrt[4]{\frac{2}{\pi}} \frac{1}{r_0^{5/2}} r e^{-1/2(r/r_0)^2}. \tag{4.5}$$

Thus, we obtain further

$$\bar{g}^2 = g^2 2^2 \sqrt{2\pi} \frac{1}{r_0^5} \tag{4.6}$$

and

$$\omega^2 = \frac{\sqrt{2}}{2^3} \left(\frac{c}{r_0} \right)^2 (\mu^2 r_0^2 - 2). \tag{4.7}$$

From (4.2), (4.6) and (4.7) we obtain

$$\frac{(G/c)^2}{4\pi\hbar c} = \frac{(2\varkappa_N g/c)^2}{4\pi\hbar c} = \frac{526}{2^6 \pi^{3/2}} \frac{\varkappa_e \varkappa_N^2}{\mu} f^3 (f^2 - 2) = 0.6097 f^3 (f^2 - 2), \tag{4.8}$$

where $G = 2\varkappa_N g$ is the constant of pseudoscalar coupling, $\varkappa_e = m_e c/\hbar$, $\varkappa_N = M_N c/\hbar$, $\mu = m_\pi c/\hbar$ ($m_\pi = 276\, m_e$), and $r_0 = f/\mu$. In order to obtain for G the experimental value deduced from the scattering of pions on nucleons $(G/c)^2/4\pi\hbar c \approx 16$ we must put in (4.8) $f \approx 2.15$.

From (4.2) and (4.7) we obtain

$$\frac{\bar{g}^2/\omega^2}{\hbar\omega} = 526 \sqrt{2} \frac{\varkappa_e}{\mu} \frac{f}{\sqrt{f^2 - 2}} = 2.268 \frac{f}{\sqrt{f^2 - 2}}. \tag{4.9}$$

For the value $f \approx 2.15$, we have $(\bar{g}/\omega)(\hbar\omega)^{1/2} \approx \sqrt{3.0}$.

In this way we see that the order of magnitude of g needed by our theory to obtain the masses of barions agrees with that deduced from scattering, if we use a "reasonable" shape of the meson cloud around the bare nucleon. We note that the value $(\bar{g}/\omega)^2/\hbar\omega = 3$, at which we achieve the above agreement. leads at the same time to zero value for the unobservable self mass $M_N - M$ of the physical nucleon (N):

$$M_N = M_1 = M + \frac{9}{2} \frac{\hbar\omega}{c^2} - \frac{3}{2} \frac{\bar{g}^2}{\omega^2 c^2} = M$$

if we do not omit the zero point energy $(9/2)\hbar\omega$.

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THEORETICAL PHYSICS

Discontinuities of Field Derivatives and Radiation in Covariant Theories

by

A. TRAUTMAN

Presented by L. INFELD on November 24, 1956

The purpose of this paper is to investigate possible forms of discontinuities of field derivatives, and their connexion with the problem of radiation and geometrical optics. In sec. 1, we briefly recall the Cauchy problem and the notion of characteristic surfaces for systems of partial differential equations. Section 2 is devoted to the general theory of discontinuities of the second derivatives of field potentials. This theory is then applied to the electromagnetic (sec. 3) and gravitational (sec. 4) fields. A close relation between the jump conditions in a linear theory and the "geometrical optics" is demonstrated in sec. 5. Covariant notation is used throughout, being essentially the same as in [1]; $\psi_A(x^\nu)$ denotes a tensor field (potentials); Greek indices run from 0 to 3, block Roman — from 1 to N; $\varphi_{[\alpha\beta]} \equiv \varphi_{\alpha\beta} - \varphi_{\beta\alpha}$; repetition of indices implies summation; the ordinary derivative is denoted by a comma ($\partial\psi_A/\partial x^\nu = \psi_{A,\nu}$).

The covariant field equations are supposed to be derivable from a variational principle: $\delta\int d_4x\sqrt{-g}\,L(g_{\mu\nu}, g_{\mu\nu,\varrho}, \psi_A, \psi_{A,\nu}) = 0$, where $g_{\mu\nu}$ is the metric tensor of the Riemannian space-time and $g = \det(g_{\mu\nu})$. Then the field equations are

$$\sqrt{-g}\,L^A = \partial\sqrt{-g}\,L/\partial\psi_A - (\partial\sqrt{-g}\,L/\partial\psi_{A,\nu})_{,\nu} = 0. \tag{1}$$

1. Since the second derivatives of the ψ's enter L^A linearly, we can write (1) in the form:

$$L^A = L^{AB\varrho\sigma}\psi_{B,\varrho\sigma} + \ldots = 0, \tag{2}$$

where $L^{AB\varrho\sigma} = -\frac{1}{2}(\partial^2 L/\partial\psi_{A,\varrho}\partial\psi_{B,\sigma} + \partial^2 L/\partial\psi_{A,\sigma}\partial\psi_{B,\varrho})$ and the dots stand for terms not containing $\psi_{A,\mu\nu}$. Let $\varphi(x^\nu) = 0$ be the equation of a hypersurface S, on which the Cauchy data are to be prescribed. This means

that we give on S (in a consistent manner, [8]) the values of ψ_A and $\psi_{A,\nu}$. Introducing a new co-ordinate system $x^{\nu'} = x^{\nu'}(x^\alpha)$, such that $x^{0'} = \varphi(x^\alpha)$, we obtain from (2):

$$L^A = L^{AB\varrho\sigma}\varphi_{,\varrho}\varphi_{,\sigma}\psi_{B,0'0'} + \text{terms not involving } \psi_{B,0,0'}.$$

The possibility of evaluating the derivatives $\psi_{A,0'0'}$ from (3) depends on the rank R of the N-th order matrix $\Lambda^{AB} = L^{AB\varrho\sigma}\varphi_{,\varrho}\varphi_{,\sigma}$. Denoting by M the maximum of this rank in a fixed point of space, $M = \max_{\varphi,\alpha} R(\Lambda^{AB})$, we have always $M \leqslant N$.

If $M = N$ and if S is such that $R(\Lambda^{AB}) = M$ on S, then the Cauchy problem formulated on S has a unique solution in the neighbourhood of S. Example: the scalar wave-equation $(\sqrt{-g}\, g^{\mu\nu}\psi_{,\nu})_{,\mu} / \sqrt{-g} + \varkappa^2\psi = 0$ and S such that $g^{\mu\nu}\varphi_{,\mu}\varphi_{,\nu} \neq 0$.

If $M < N$, the field equations (1) are underdetermined, and for no S have a unique solution. Additional conditions must be added in order to ensure uniqueness. Examples: Maxwell's and Einstein's equations.

A hypersurface S on which $R(\Lambda^{AB}) < M \leqslant N$ is called *characteristic*. The initial value problem cannot be correctly formulated on a characteristic hypersurface.

2. The existence of solutions with discontinuous derivatives is known to be closely related to the hyperbolic character of field equations. A discontinuous solution represents a disturbance of the field propagating with a finite velocity and can be interpreted as radiation.

Our field equations (1) being of the second order, we assume that the ψ's and their first derivatives are continuous throughout and that $\psi_{A,\mu\nu}$ are continuous everywhere except on hypersurface $S(\varphi = 0)$. Denoting by $\Delta\psi_{A,\mu\nu}$ the jump of $\psi_{A,\mu\nu}$ across S, we have, from purely geometrical considerations [2],

$$\Delta\psi_{A,\mu\nu} = \eta_A\varphi_{,\mu}\varphi_{,\nu}; \tag{3}$$

where η_A is a tensor field defined on S.

The field equations being valid everywhere, we obtain from (2):

$$L^{AB\varrho\sigma}\Delta\psi_{B,\varrho\sigma} = 0 \text{ on } S,$$

or

$$\Lambda^{AB}\eta_B = 0 \qquad (A = 1, \ldots, N). \tag{4}$$

The jumps of $\psi_{A,\mu\nu}$ can appear only on such S for which

$$\det(\Lambda^{AB}) = 0. \tag{5}$$

Thus $\psi_{A,\mu\nu}$ can be discontinuous 1° on any surface when (1) are underdetermined; 2° on a characteristic surface. Examples given below show that only the latter jumps have a physical meaning.

3. In the *electromagnetic* theory the ψ's must be replaced by a vector-potential A_α. The field equations are $L^\alpha = (\sqrt{-g}\, f^{\alpha\beta})_{,\beta}/\sqrt{-g} = 0$, where $f_{\alpha\beta} \equiv A_{[\beta,\alpha]}$. $L^{AB\varrho\sigma}$ becomes $L^{\alpha\beta\varrho\sigma} = \frac{1}{2}(g^{\alpha[\varrho}g^{\beta]\sigma} + g^{\alpha[\sigma}g^{\beta]\varrho})$ and the matrix Λ^{AB}:

$$\Lambda^{\alpha\beta} = \varphi^{,\alpha}\varphi^{,\beta} - g^{\alpha\beta}\varphi_{,\nu}\varphi^{,\nu}. \tag{6}$$

We get for the rank of (6):

$$R(\Lambda^{\alpha\beta}) = \begin{cases} 3 = M < N = 4 & \text{for} \quad \varphi_{,\nu}\varphi^{,\nu} \neq 0, \quad \text{(a)} \\ 1 & \text{for} \quad \varphi_{,\nu}\varphi^{,\nu} = 0. \quad \text{(b)} \end{cases}$$

The Maxwell equations are underdetermined, and their characteristic surfaces coincide with null surfaces [4]. Writing b_α for η_A we have $\Delta A_{\alpha,\mu\nu} = b_\alpha \varphi_{,\mu}\varphi_{,\nu}$.

In case (a), equation (4) leads to

$$(\varphi^{,\alpha}\varphi^{,\beta} - g^{\alpha\beta}\varphi_{,\nu}\varphi^{,\nu})\, b_\beta = 0. \tag{7}$$

The general solution of (7) is $b_\alpha = b\varphi_{,\alpha}$ (b = scalar function); then $\Delta A_{\alpha,\mu\nu} = b\varphi_{,\alpha}\varphi_{,\mu}\varphi_{,\nu}$. But such jumps have no physical significance:

$$\Delta f_{\alpha\beta,\gamma} = \Delta(A_{\beta,\alpha\gamma} - A_{\alpha,\beta\gamma}) = 0. \tag{8}$$

In case (b), we have $\varphi_{,\nu}\varphi^{,\nu} = 0$, and (4) leads to

$$b^\alpha \varphi_{,\alpha} = 0. \tag{9}$$

The corresponding jumps in field strength derivatives are

$$\Delta f_{\dot{\alpha}\beta,\gamma} = b_{[\beta}\varphi_{,\alpha]}\varphi_{,\gamma}. \tag{10}$$

Introducing electric $\vec{E}$ and magnetic $\vec{H}$ field strengths, we can write (9), (10) in vector notation:

$$\Delta\vec{E}_{,\gamma} = \varphi_{,\gamma}\vec{e}, \qquad \Delta\vec{H}_{,\gamma} = \varphi_{,\gamma}\vec{n} \times \vec{e}, \qquad \vec{n} \cdot \vec{e} = 0,$$

where $\varphi_{,0}\vec{n} = \operatorname{grad}\varphi$, $e_k = \varphi_{,0}(b_k - n_k b_0)$. The jumps $\Delta\vec{E}_{,\gamma}$ and $\Delta\vec{H}_{,\gamma}$ can be called "weak" in contradistinction to "strong" discontinuities of $\vec{E}$ and $\vec{H}$ (i. e., of the *first* derivatives of the potential). Strong discontinuities of the electromagnetic field were examined by Rubinowicz [3].

4. In Einstein's general relativity, the potentials ψ_A of the *gravitational* field are identified with the metric tensor $g_{\alpha\beta}$. Field equations *in vacuo* are $R_{\alpha\beta} = 0$, where $R_{\alpha\beta} = g^{\mu\nu}R_{\alpha\mu\beta\nu}$, and $R_{\alpha\beta\gamma\delta}$ denotes the Riemann curvature tensor of the space-time.

The Cauchy problem and jump conditions for the gravitational field have been investigated by several authors [4]–[7]; we give a detailed and co-variant expression for the jumps of the curvature tensor.

According to Lichnerowicz [4], we assume that there exists a co-ordinate system in which $g_{\alpha\beta}$, $g_{\alpha\beta,\gamma}$ are continuous and $g_{\alpha\beta,\gamma\delta}$ are piece-

wise continuous. Co-ordinate transformations $x^\nu \to x^{\nu'}$ are assumed to be of class C^3. Denoting the jump of $g_{\alpha\beta,\gamma\delta}$ across S by $\Delta g_{\alpha\beta,\gamma\delta}$, we note that this is a *tensor* field on S. Indeed, in virtue of $\Delta g_{\alpha\beta}=0$, $\Delta g_{\alpha\beta,\gamma}=0$, $\Delta \partial x^\nu/\partial x^{\nu'}=0$, etc., we have ($A^\nu_{\gamma'}=\partial x^\nu/\partial x^{\gamma'}$):

$$\Delta g_{\alpha'\beta',\gamma'\delta'}=\Delta[((g_{\alpha\beta}A^\alpha_{\alpha'}A^\beta_{\beta'})_{,\gamma}A^\gamma_{\gamma'})_{,\delta}A^\delta_{\delta'}]=A^\alpha_{\alpha'}A^\beta_{\beta'}A^\gamma_{\gamma'}A^\delta_{\delta'}\Delta g_{\alpha\beta,\gamma\delta}.$$

It follows from (3) that

$$\Delta g_{\alpha\beta,\gamma\delta}=h_{\alpha\beta}\varphi_{,\gamma}\varphi_{,\delta} \qquad (h_{\alpha\beta}=h_{\beta\alpha} \text{ is a tensor}). \tag{11}$$

Latin indices $A,B,\ldots$ must be identified with the 10 (symmetric) pairs $(\alpha\beta),(\gamma\delta),\ldots$ The symbol $L^{AB\varrho\sigma}$ becomes

$$L^{(\alpha\beta)(\gamma\delta)\varrho\sigma}=\tfrac{1}{8}(g^{\alpha[\gamma}g^{\sigma]\varrho}g^{\varrho[\delta}g^{\sigma]\beta}+g^{\alpha[\delta}g^{\sigma]\varrho}g^{\varrho[\gamma}g^{\sigma]\beta}+g^{\alpha[\gamma}g^{\varrho]\sigma}g^{\sigma[\delta}g^{\varrho]\beta}+g^{\alpha[\delta}g^{\varrho]\sigma}g^{\sigma[\gamma}g^{\varrho]\beta}).$$

The 0th order matrix $\Lambda^{AB}=\Lambda^{(\alpha\beta)(\gamma\delta)}=L^{(\alpha\beta)(\gamma\delta)\varrho\sigma}\varphi_{,\varrho}\varphi_{,\sigma}$ has the rank [5]:

$$R(\Lambda^{(\alpha\beta)(\gamma\delta)})=\begin{cases}6=M<N=10 & \text{for} \quad \varphi_{,\nu}\varphi^{,\nu}\neq 0, \quad \text{(a)}\\ 4 & \text{for} \quad \varphi_{,\nu}\varphi^{,\nu}=0. \quad \text{(b)}\end{cases}$$

The Einstein equations are underdetermined (general covariance); to them must be added 4 conditions fixing the co-ordinate system.

In case (a), equation (4) implies

$$(\delta^\mu_\alpha\varphi_{,\beta}\varphi^{,\nu}+\delta^\mu_\beta\varphi_{,\alpha}\varphi^{,\nu}-\delta^\mu_\alpha\delta^\nu_\beta\varphi_{,\varrho}\varphi^{,\varrho}-g^{\mu\nu}\varphi_{,\alpha}\varphi_{,\beta})h_{\mu\nu}=0. \tag{12}$$

The general solution of (12) can be easily found:

$$h_{\alpha\beta}=h_\alpha\varphi_{,\beta}+h_\beta\varphi_{,\alpha} \qquad (h_\alpha - \text{arbitrary vector field}),$$

but the corresponding jumps of the curvature tensor vanish:

$$\Delta R_{\alpha\beta\gamma\delta}=\tfrac{1}{2}(\Delta g_{\alpha\delta,\beta\gamma}+\Delta g_{\beta\gamma,\alpha\delta}-\Delta g_{\alpha\gamma,\beta\delta}-\Delta g_{\beta\delta,\alpha\gamma})=0.$$

Equation (4) leads, in case (b), to

$$h_\alpha{}^\nu\varphi_{,\nu}\varphi_{,\beta}+h_\beta{}^\nu\varphi_{,\nu}\varphi_{,\alpha}-h_\nu{}^\nu\varphi_{,\alpha}\varphi_{,\beta}=0. \tag{13}$$

Among the 10 equations (13), only 4 are independent. Thus, in an arbitrary co-ordinate system, $h_{\alpha\beta}$ has 6 components algebraically independent. The corresponding discontinuities of the Riemann tensor are:

$$\Delta R_{\alpha\beta\gamma\delta}=\tfrac{1}{2}\varphi_{,[\alpha}h_{\beta][\gamma}\varphi_{,\delta]}. \tag{14}$$

Let us summarise: the curvature tensor $R_{\alpha\beta\gamma\delta}$ of empty space-time can be discontinuous only on null surfaces ($\varphi_{,\nu}\varphi^{,\nu}=0$). The jump of $R_{\alpha\beta\gamma\delta}$ is defined at each point by six numbers and has the form (14). The analogy with electrodynamics allows us to consider pure gravitational fields with discontinuous Riemann tensor as representing gravitational radiation [7].

5. Let us restrict ourselves to linear field theories. Solutions of the form $\psi_A = \eta_A e^{i\omega\varphi(x)}$, where ω is a great number, represent, in the electromagnetic case, light (optical) waves. Extending the notion of *geometrical optics* to any linear field theory, we can obtain an "eikonal" equation as follows. Introducting $\psi_A = \eta_A e^{i\omega\varphi}$ in (2), and disregarding terms not containing ω^2 we obtain:

$$-\omega^2 L^{AB\varrho\sigma}\eta_B\varphi_{,\varrho}\varphi_{,\sigma} = 0,$$

i. e., an equation identical in form with (4). Thus (5) is again a necessary and sufficient condition for the existence of a non-vanishing amplitude η_A. The condition

$$R(\Lambda^{AB}) < M$$

can be called, by analogy with electrodynamics, an *eikonal equation*. These few remarks again reveal the connexion between propagation of discontinuities and wave phenomena *).

The author is greatly indebted to Professor L. Infeld for his kind interest in this paper.

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*) *Note added in proof.* From the condition $R(\Lambda^{AB}) < M$ defining the characteristic surfaces, we can also obtain the velocity (or velocities) v of propagation of the disturbances. For Maxwell's theory this is trivial: $g^{\mu\varrho}\varphi_{,\mu}\varphi_{,\nu} = 0$ implies $v = c$. But if we take, e. g., a non-linear electrodynamics, then we get, apart $v = c$, several different velocities, depending on the field strengths.

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THEORETICAL PHYSICS

On the Energy-Momentum Tensor Density for Simple Pole Particles

by

W. TULCZYJEW

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1. The object of the present paper is to show that the form of the energy-momentum tensor density for a system of simple pole particles, which we shall assume to be a linear function of δ, is completely determined by the field equations of the general relativity theory.

The problem of deducing covariant equations of motion for a system of simple pole particles from the field equations was solved by L. Infeld and J. Plebański [1]. It was shown that these equations of motion can be put in the form of "geodetic line" equations, by which we mean

$$\overset{a}{\xi}{}''^{\alpha} + \left\{ \begin{matrix} \tilde{\alpha} \\ \varrho\sigma \end{matrix} \right\} \overset{a}{\xi}{}'^{\varrho} \overset{a}{\xi}{}'^{\sigma} = 0,$$

where $\overset{a}{\xi}{}'^{\alpha} = d\overset{a}{\xi}{}^{\alpha}/d\overset{a}{\tilde{s}}$, $d\overset{a}{\tilde{s}} = (\tilde{g}_{\alpha\beta} d\overset{a}{\xi}{}^{\alpha} d\overset{a}{\xi}{}^{\beta})^{1/2}$, the operation "$\sim$" is defined by $\overset{a}{\tilde{f}}(t) = \int f(x^s, t)\, \hat{\delta}(x^r - \overset{a}{\xi}{}^r(t))\, d_{(3)}x$ and $\overset{a}{\xi}{}^{\alpha}$ are the co-ordinate of a-th particle. $\hat{\delta}$ and its generalisation $\hat{\tilde{\delta}}$ were introduced by L. Infeld and J. Plebański in [2] and [3]. In what follows we shall write for short $\overset{a}{\delta}$ instead of $\hat{\delta}(x^s - \overset{a}{\xi}{}^s)$.

Let us formulate the assumptions adopted in [1].

a. The operation "$\sim$" was assumed to be distributive with respect to multiplication when applied to gravitational field and its derivatives, e. g.:

$$\tilde{g}^{\alpha\beta}[\widetilde{\nu\mu, \beta}] = \left\{ \begin{matrix} \tilde{\alpha} \\ \nu\mu \end{matrix} \right\}.$$

This is not the case with arbitrary functions. More about this problem can be found in [4]. We shall make use of this important assumption also in the present paper.

b. Energy-momentum tensor density was given the special form

$$T^{\alpha\beta}=\sum_{a} m_0^{a}\dot{\xi}^{a\alpha}\dot{\xi}^{a\beta}\delta^{a}=\sum_{a} m_0^{a}\frac{d\tilde{s}^{a}}{dt}\xi'^{a\alpha}\xi'^{a\beta}\delta^{a};\qquad \dot{\xi}^{a\alpha}=\frac{d\xi^{a\alpha}}{dt}$$

and the scalars m_0 were assumed to have constant values.

We replace this by

$$T^{\alpha\beta}=\sum_{a} t^{a\alpha\beta}\delta^{a},$$

which is the most general form in the case considered. Equations

(1) $$\frac{dt}{d\tilde{s}}t^{\alpha\beta}=m_0\xi'^{\alpha}\xi'^{\beta}$$

and

$$\frac{dm_0}{d\tilde{s}}=0$$

will be deduced from the field equations by means of a method which we shall now develop. We shall discuss the case of one body only, the generalisation to the case of several bodies being trivial.

2. Let us start with a covariant equation which is a consequence of the field equations and Bianchi identities,

(2) $$\frac{dt}{d\tilde{s}}\int\theta T^{\alpha\beta}{}_{;\beta}\,d_{(3)}x=0,$$

with θ an arbitrary scalar field. $T^{\alpha\beta}{}_{;\beta}$ can be expressed as follows:

$$T^{\alpha\beta}{}_{;\beta}=t^{\alpha\nu}\delta_{,\nu}+(t^{\alpha 0}\delta)_{,0}+\left\{\begin{matrix}\alpha\\ \varrho\sigma\end{matrix}\right\}t^{\varrho\sigma}\delta=\left(t^{\alpha 0}{}_{,0}+\left\{\begin{matrix}\alpha\\ \varrho\sigma\end{matrix}\right\}t^{\varrho\sigma}\right)\delta+(t^{\alpha\nu}-t^{\alpha 0}\dot{\xi}^{\nu})\,\delta_{,\nu}.$$

Introducing this into (2) and adopting the definitions,

$$\frac{dt}{d\tilde{s}}\left(t^{\alpha 0}{}_{,0}+\left\{\begin{matrix}\alpha\\ \varrho\sigma\end{matrix}\right\}t^{\varrho\sigma}\right)=A^{\alpha}$$

and

$$\frac{dt}{d\tilde{s}}(t^{\alpha\beta}-t^{\alpha 0}\dot{\xi}^{\beta})=A^{\alpha\beta}\qquad A^{\alpha 0}=0,$$

we obtain, by performing the integration,

$$\overline{\theta A^{\alpha}}-\overline{\theta_{,\beta}A^{\alpha\beta}}=0.$$

And since θ is an arbitrary function we have

(3) $$\tilde{A}^{\alpha}=0$$

and

$$\tilde{A}^{\alpha\beta}=0.$$

The last equation written out explicitly for $\alpha \to 0$, $\beta \to \alpha$ gives

$$\tilde{A}^{0\alpha} = \frac{dt}{d\tilde{s}}(t^{\alpha 0} - t^{00}\dot{\xi}^{\alpha}) = 0,$$

hence

$$t^{\alpha 0} = t^{00}\dot{\xi}^{\alpha}.$$

Denoting the scalar $\frac{d\tilde{s}}{dt}t^{00}$ by m_0 we have

$$t^{\alpha 0} = m_0 \xi'^{\alpha} \tag{4}$$

and

$$\tilde{A}^{\alpha\beta} = \frac{dt}{d\tilde{s}}t^{\alpha\beta} - m_0 \xi'^{\alpha}\xi'^{\beta} = 0, \tag{5}$$

which is equivalent to (1). We can now transform $\tilde{A}^{\alpha}$ according to (4) and (5),

$$\tilde{A}^{\alpha} = \frac{d}{d\tilde{s}}(m_0 \xi'^{\alpha}) + m_0 \left\{ \begin{matrix} \tilde{\alpha} \\ \varrho\sigma \end{matrix} \right\} \xi'^{\varrho}\xi'^{\sigma}. \tag{6}$$

We shall need some auxiliary formulae. The definition of $d\tilde{s}$ leads to

$$\tilde{g}_{\alpha\beta}\xi'^{\alpha}\xi'^{\beta} = 1. \tag{7}$$

Differentiation gives

$$\frac{d\tilde{g}_{\alpha\beta}}{d\tilde{s}}\xi'^{\alpha}\xi'^{\beta} + 2\tilde{g}_{\alpha\beta}\xi''^{\alpha}\xi'^{\beta} = 0.$$

The first term of the above formula can be calculated as follows:

$$\frac{d\tilde{g}_{\alpha\beta}}{d\tilde{s}}\xi'^{\alpha}\xi'^{\beta} = \xi'^{\alpha}\xi'^{\beta}\frac{d}{d\tilde{s}}\int g_{\alpha\beta}\delta\, d_{(3)}x = \xi'^{\alpha}\xi'^{\beta}\frac{dt}{d\tilde{s}}\int (g_{\alpha\beta,0}\delta - g_{\alpha\beta}\dot{\xi}^{r}\delta_{,r})\, d_{(3)}x =$$

$$= \widetilde{g_{\alpha\beta,\gamma}}\xi'^{\alpha}\xi'^{\beta}\xi'^{\gamma} = 2\tilde{g}_{\alpha\varrho}\left\{ \begin{matrix} \tilde{\varrho} \\ \beta\gamma \end{matrix} \right\} \xi'^{\alpha}\xi'^{\beta}\xi'^{\gamma},$$

hence

$$2\tilde{g}_{\alpha\beta}\left(\xi''^{\alpha} + \left\{ \begin{matrix} \tilde{\alpha} \\ \varrho\sigma \end{matrix} \right\} \xi'^{\varrho}\xi'^{\sigma}\right)\xi'^{\beta} = 0. \tag{8}$$

Because of (6), (7) and (8) we have

$$\tilde{g}_{\alpha\beta}\tilde{A}^{\alpha}\xi'^{\beta} = \frac{dm_0}{d\tilde{s}}.$$

This leads by virtue of (3) and (6) to

$$\frac{dm_0}{d\tilde{s}} = 0$$

and

$$\xi''^{\alpha} + \left\{ \begin{matrix} \tilde{\alpha} \\ \varrho\sigma \end{matrix} \right\} \xi'^{\varrho}\xi'^{\sigma} = 0.$$

3. Let us summarise the results. First we have

$$\frac{dt}{d\tilde{s}}t^{\alpha\beta} = m_0 \xi'^{\alpha} \xi'^{\beta}.$$

This means that the only characteristic quantity of the particle is its mass and thus there is no possibility of expressing internal structure of bodies by means of an energy-momentum tensor density which is proportional to δ. Then we see that the rest mass of the particle is constant and drops out from the final equations of motion. This important result proves the equivalence principle for particles with finite mass.

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THEORETICAL PHYSICS

Polarization of Nucleons from the Break-up of the Deuteron in the Electromagnetic Field of a Nucleus

by

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Presented by L. INFELD on January 7, 1957

The cross-section for the disintegration of the fast deuteron in flight due to the electric (Coulomb) field of a heavy nucleus has been calculated in a number of papers ([1]—[6]). However, only Kagan [5] and Rosenzweig and Sitenko [6] have so far calculated the magnetic disintegration due to the interaction of the field of the fast deuteron with the deuteron magnetic moment. For the energy $E_0 = 200$ MeV, the total magnetic cross-section was estimated by Kagan [5] for intermediate Z, in a quasiclassical manner, to be $\sigma_M \cong 3 \cdot 10^{-29} Z^2$ cm.^{2}. The corresponding total electric cross-section found by Dancoff [1] is $\sigma_{Ec} \cong 2 \cdot 10^{-29} Z^2$ cm^2. The relative importance of the magnetic effect increases with the increase of energy. Nobody has hitherto observed that the relatively weak magnetic effect appears more distinctly by way of interference with the electric effect in the spin polarization of the outgoing nucleons. At intermediate energies ($\sim$10—30 MeV), the nuclear interaction of the incident deuteron with the target nucleus results mostly for the majority of nuclei in stripping, with capture of one of the nucleons to a bound state. The electromagnetic break-up can therefore be experimentally separated with the help of neutron-proton coincidence measurements. At high energies ($\sim$100—200 MeV), the intermediate nucleus excited in a stripping act has a short life; however, it is sufficient in a number of cases to enable partial elimination of the nuclear interaction. The most important fact at high energies is, however, the sharp forward peak of the stripping nucleons (the cone is $\Delta\vartheta \sim 6°$, Serber [7]). The nucleons outgoing at much larger angles come for the most part from the electromagnetic break-up. It seems that coincidence experiments at larger angles might, together with the polarization measurements, detect and investigate the magnetic effect. The details of the non-central internal interactions of the $n-p$ sy-

stem usually have less influence on the polarization than the electric-magnetic interference [8].

The basic assumptions of Kagan [5] will be applied in the calculation. The reaction amplitude at high energies ($n_d = Ze^2/\hbar v_0 \ll 1$, v_0 being the deuteron velocity) is calculated on the stationary theory of perturbations. The interaction potential with the electromagnetic field of the nucleus is treated as the perturbation: $V = V_{El} + V_M$, where

$$(1) \qquad V_{El} = \frac{Ze^2}{\left|\vec{R} + \frac{\vec{\varrho}}{2}\right|}, \qquad V_M = -(\vec{M}\cdot\vec{H}) = -\frac{Zei\hbar}{Mc}\,\vec{M}\cdot\left(\frac{\vec{R}}{R^3}\times\nabla_R\right).$$

$\vec{R}$ is the vector from the origin (the nucleus) to the centre of mass of the deuteron, $\vec{\varrho}$ is the vector from the neutron to the proton and $\vec{M} = \frac{1}{2}(\mu_n + \mu_p)(\vec{\sigma}_n + \vec{\sigma}_p) + \frac{1}{2}(\mu_n - \mu_p)(\vec{\sigma}_n - \vec{\sigma}_p)$ is the magnetic moment of the deuteron, where $\mu_{n(p)} = \frac{e\hbar}{2Mc}\mu^0_{n(p)}$ and $\mu^0_n = -1.91$, $\mu^0_p = 2.79$; M is the nucleon mass. The approximate expression for V_M — (1) was obtained by disregarding the $n-p$ range. This seems to be satisfactory in view of the smallness of the $\vec{\varrho}$-dependent terms and the fact that the spin operators play the most important part in the magnetic interaction (a magnetic transition is a spin transition above all).

Due to the assumption $Ze^2/\hbar v_0 \ll 1$, the initial state of the system may be approximated by the function

$$\psi_0 = \frac{1}{\sqrt{v_0}} e^{i\vec{k}_0\vec{R}} D_i(\vec{\varrho})\,\chi_1^{m_0}, \qquad \text{where} \qquad D_i(\vec{\varrho}) = \sqrt{\frac{\alpha N^2}{2\pi}}\,\frac{e^{-\alpha\varrho}}{\varrho}$$

is the deuteron "zero range" internal wave function, $\alpha = \sqrt{\frac{M\epsilon}{\hbar^2}}$, ϵ = the deuteron binding energy, $N^2 \cong 3/2$ = the normalization correction factor, $\chi_1^{m_0}$ = the deuteron triplet spin function*). The ${}^3D_1$-state admixture to the ground state is disregarded. The neutron-proton central spin dependent interaction $V^S_{m_p}(\varrho)$ in the final states will be taken into account, consistently, in the "zero range" approximation. This means that the "final states" $D^S_{k_\varrho}(\vec{\varrho})\,\chi^m_S$, consisting of a plane wave plus a spherical convergent wave, satisfy the equation

$$\left(\frac{\hbar^2}{M}\Delta_\varrho + E_\varrho\right) D^S_{\vec{k}_\varrho}(\vec{\varrho})\,\chi^m_S = 0$$

with the boundary conditions

$$\frac{d}{d\varrho}\left[\ln\left[\varrho D^S_{\vec{k}_\varrho}(\vec{\varrho})\right]\right]_{|\varrho\to 0} = -\alpha_S.$$

*) Similar final expressions would be obtained by using a Hulthén function with properly modified corresponding α_s.

For the triplet states ($S=1$) $a_1=a$, and for the singlet states ($S=0$) $a_0=-\sqrt{\frac{M\epsilon_0}{\hbar^2}}$, where ϵ_0 = the energy of the virtual state of the deuteron. If the "final states" are normalized to $\delta(\vec{k}_\varrho-\vec{k}'_\varrho)$, where $\frac{\hbar^2k_\varrho^2}{M}=E_\varrho$, they may be written in the form

$$D^S_{\vec{k}_\varrho}(\vec{\varrho})\chi^m_S=\frac{1}{(2\pi)^{3/2}}\left(e^{i\vec{k}_\varrho\vec{\varrho}}+\beta^*_S\frac{e^{-ik_\varrho\varrho}}{ik_\varrho\varrho}\right)\chi^m_S, \tag{2}$$

where $\beta^*_S=ik_\varrho/(ik_\varrho-a_S)$. The distortion coefficient $\beta_S=ik_\varrho/(ik_\varrho+a_S)=\frac{1-\eta_S}{2}=\frac{1-e^{i2\delta_S}}{2}$, where the phase shift δ_S is given by $e^{i\delta_S}=\frac{ik_\varrho-a_S}{\sqrt{k_\varrho^2+a_S^2}}$. In general, for a_S stand the values corresponding to a particular spin dependent central potential. In the case of no final state interaction, the "final states" and the initial state are, of course, orthogonal. It is easy to ascertain that $\int D^{1*}_{\vec{k}_\varrho}(\vec{\varrho})D_i(\vec{\varrho})d\vec{\varrho}=0$. The motion of the centre of mass of the deuteron is described by the function $\psi_{\vec{K}}(\vec{R})=\frac{1}{(2\pi)^{3/2}}e^{i\vec{K}\vec{R}}$, where $\frac{\hbar^2K^2}{4M}=E_R$.

The wave function representing the solution of the collision problem has the asymptotical form

$$\Psi_{n-p}(\vec{R},\vec{\varrho};\sigma)\sim\int d\vec{k}_\varrho\frac{e^{ikR}}{R}|f\rangle, \tag{3}$$

$$|f\rangle=\sum_{S,m}\langle\vec{k}_\varrho,\vec{k};\,s,m\,|V_{El}+V_M|i,\vec{k}_0;\,1,m_0\rangle D^S_{\vec{k}_\varrho}(\vec{\varrho})\chi^m_S, \tag{4}$$

where, due to the conservation of energy (resulting from the $\vec{k}$-integration), $E_R+E_\varrho=E_0-\epsilon=\frac{\hbar^2k_0^2}{4M}-\epsilon=E_n+E_p$, where $E_{n(p)}$ is the energy of the neutron (proton) in the final state. The electric transitions are only to $S=1$ (with δ_{mm_0}), and the magnetic ones only to $S=0$. Eq. (4) may be rewritten in the form

$$|f\rangle=\langle\vec{k}_\varrho,\vec{k};\,s,m=m_0|V_{El}|i,\vec{k}_0;\,1,m_0\rangle D^1_{\vec{k}_\varrho}(\vec{\varrho})\chi_1^{m=m_0}+ \tag{5}$$

$$+\langle\vec{k}_\varrho,\vec{k};\,0,0|V_M|i,\vec{k}_0;\,1,m_0\rangle D^0_{\vec{k}_\varrho}(\vec{\varrho})\chi^0_0.$$

On multiplying (3) by its complex conjugate, integrating over $\vec{\varrho}$ and σ and then averaging over m_0, we obtain, due to the relation $\int D^{S*}_{\vec{k}_\varrho}(\vec{\varrho})D^{S'}_{\vec{k}_\varrho}(\vec{\varrho})d\vec{\varrho}=\delta(\vec{k}_\varrho-\vec{k}'_\varrho)$ (independent of S,S'), the differential cross-

section

$$(6)\qquad \frac{d\sigma}{d\Omega_{\vec{k}}} \propto \int d\vec{k}_\varrho \{ |\langle \vec{k}_\varrho, \vec{k};\, 1, m_0 | V_{El} | i, \vec{k}_0;\, 1, m_0 \rangle|^2 + \frac{1}{3} |\langle \vec{k}_\varrho, \vec{k};\, 0, 0 | V_M | i, \vec{k}_0;\, 1, m_0 = \overline{m}_0 \rangle|^2 \},$$

where $\overline{m}_0$ is the only value of m_0 contributing to $\langle |V_M| \rangle$. Let us calculate $\langle |V_{El}| \rangle$ and $\langle |V_M| \rangle$, and see how then to choose the system of reference enabling a simple calculation of the polarization. Omitting the unimportant (for the sake of polarization) coefficients, we have

$$(7)\qquad f_{El}(\vec{s}, \vec{k}_\varrho) = \int d\vec{\varrho} d\vec{R} e^{-i\vec{k}\vec{R}} \left(e^{-i\vec{V}_\varrho \vec{\varrho}} - \beta_1 \frac{e^{ik_\varrho \varrho}}{ik_\varrho \varrho} \right) \frac{Ze^2}{\left| \vec{R} + \frac{\vec{\varrho}}{2} \right|} e^{i\vec{k}_0 \vec{R}} \frac{e^{-\alpha\varrho}}{\varrho} \cong$$

$$\cong -(4\pi)^2 \frac{Ze^2 k_\varrho \cos\gamma}{s(k_\varrho^2 + \alpha^2)},$$

where $\vec{s} = \vec{k}_0 - \vec{k}$, $\gamma = \sphericalangle(s, \vec{k})$. Eq. (7) was obtained in the dipole approximation. (One can either pass to the variables $\vec{\varrho}$ and $\vec{r}_p = \vec{R} + \frac{\vec{\varrho}}{z}$ and use them (Kagan [5]) or replace Ze^2/r_p by the first, i. e., the dipole term $= -Ze^2(\vec{R}\cdot\vec{\varrho})/R^3$ (Guth and Mullin [3]); in both cases we obtain the same result *)).

The magnetic matrix element is

$$(8)\qquad f_M^{m_0}(\vec{s}, \vec{k}_\varrho) =$$

$$= \int d\vec{\varrho} d\vec{R} d\sigma e^{-i\vec{k}\vec{R}} \left(e^{-i\vec{k}_\varrho \vec{\varrho}} - \beta_0 \frac{e^{ik_\varrho \varrho}}{ik_\varrho \varrho} \right) \chi_0^{0*} \left(-\frac{Zei\hbar}{cM} \vec{M} \cdot \left(\frac{\vec{R}}{R^3} \times \nabla_R \right) \right) e^{i\vec{k}_0 \vec{R}} \frac{e^{-\alpha\varrho}}{\varrho} \chi_1^m.$$

It can easily be shown (e. g. in analogy to Kagan [5]) that:

$$(9)\qquad f_M^{m_0}(\vec{s}, \vec{k}_\varrho) = -(4\pi)^2 \frac{Zei\hbar}{2Mc} (\mu_n - \mu_p) \frac{\alpha_0 - \alpha}{(k_\varrho^2 + \alpha^2)(ik_\varrho + \alpha_0)} \frac{[\vec{k}_0 \times \vec{s}]}{s^2} \int d\sigma \chi_0^{0*} (\vec{\sigma}_n - \vec{\sigma}_p) \chi_1^{m_0}.$$

If we choose the quantization axis, $Oz \| \vec{k}_0 \times \vec{s} = \vec{k} \times \vec{k}_0$, then $\overline{m}_0 = 0$ and $(\int d\sigma \ldots)_z = 1$. We then obtain

$$(10)\qquad f_M^{m_0}(\vec{s}, \vec{k}_\varrho) = \delta_{0m_0} f_M = -\delta_{0m_0} (4\pi)^2 \frac{Zei\hbar}{2Mc} (\mu_n - \mu_p) \frac{\alpha_0 - \alpha}{(k_\varrho^2 + \alpha^2)(ik_\varrho + \alpha)} \frac{|\vec{k} \times \vec{k}_0|}{s^2}.$$

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*) We can estimate the quadrupole term as small. The full interaction gives the (exact) formula

$$f_{El}(\vec{s}, \vec{k}_\varrho) = \frac{(4\pi)^2}{s^2} \left(1/\alpha^2 + \left(k_\varrho + \frac{s}{2} \right)^2 \right) - \frac{\beta_1}{ik_\varrho s} \left[\operatorname{arc\,tg} \left(\frac{\frac{s}{2} - k_\varrho}{\alpha} \right) + \operatorname{arc\,tg} \left(\frac{\frac{s}{2} + k_\varrho}{\alpha} \right) + \frac{i}{2} \ln \frac{\left(\frac{s}{2} - k_\varrho \right)^2 + \alpha^2}{\left(\frac{s}{2} + k_\varrho \right)^2 + \alpha^2} \right].$$

It can easily be proved that this system of reference is the most convenient, also, for calculation of the polarization. The expression in (3) becomes

$$\int d\vec{k}_\varrho \frac{e^{ikR}}{R}|f\rangle \doteq \int d\vec{k}_\varrho \frac{e^{ikR}}{R}\{f_{El} D^1_{\vec{k}_\varrho}(\vec{\varrho})\chi_1^{m_0} + \delta_{0m_0} f_M D^0_{\vec{k}_\varrho}(\vec{\varrho})\chi_0^0\}. \tag{11}$$

On working with the operator of the neutron spin $\vec{\sigma}_n$ on the left, multiplying the result by the complex conjugate to (11), integrating over $\vec{\varrho}$, σ, multiplying by R^2 and averaging over m_0, we obtain, as in the case of $d\sigma/d\Omega_{\vec{k}}$,

$$\int d\vec{k}_\varrho \tfrac{1}{3}\sum_{m_0}\int d\sigma[f_{El}\chi_1^{m_0} + \delta_{0m_0} f_M \chi_0^0]^* \vec{\sigma}_n [f_{El}\chi_1^{m_0} + \delta_{0m_0} f_M \chi_0^0]. \tag{12}$$

In the chosen system of reference, the x- and y-components of the vector (12) vanish, and the z-component is

$$\int d\vec{k}_\varrho \tfrac{2}{3} Re[f_{El} f_M^*].$$

If E_n and both the angles of the outgoing neutron and proton in the reaction plane are measured experimentally, then $\vec{k}_\varrho$ and $\vec{k}$ are fixed. In this case, we obtain the degree of the neutron polarization:

$$P = P_z(\vec{k}_\varrho, \theta_{\vec{k}}) = \frac{\frac{2}{3} Re[f_{El}(\vec{s},\vec{k}_\varrho) f_M^*(\vec{s},\vec{k}_\varrho)]}{|f_{El}(\vec{s},\vec{k}_\varrho)|^2 + \frac{1}{3}|f_M(\vec{s},\vec{k}_\varrho)|^2}. \tag{13}$$

The polarization in the reaction plane is zero ($P_x \equiv P_y \equiv 0$). Substituting of (7) and (10) into (13) gives, after simple transformations:

$$P = \frac{\frac{1}{6}\lambda^2(\mu_p^0 - \mu_n^0)(\alpha - \alpha_0)\left\{\frac{k_\varrho^2 |\vec{k}\times\vec{k}_0|\cos\gamma}{s(k_\varrho^2+\alpha^2)(k_\varrho^2+\alpha_0^2)}\right\}}{\frac{k_\varrho^2\cos^2\gamma}{(k_\varrho^2+\alpha^2)^2} + \frac{1}{48}\lambda^4(\mu_p^0-\mu_n^0)(\alpha-\alpha_0)^2\left\{\frac{|\vec{k}\times\vec{k}_0|^2}{s^2(k_\varrho^2+\alpha_0^2)}\right\}}, \tag{14}$$

where $\lambda_n = \hbar/Mc$ = the nucleon Compton wavelength. For the sake of discussion, let us pass from $\vec{k}_\varrho, \vec{k}$ to $\vec{k}_n, \vec{k}_p$ – the wave vectors of the neutron and the proton

$$E_n = \frac{\hbar^2 k_n^2}{2M},\ E_p = \frac{\hbar^2 k_p^2}{2M} = E_0 - \epsilon - E_n.$$

On denoting $\sphericalangle(\vec{k}_n, \vec{k}_p) = \theta$, $\sphericalangle(\vec{k}_n, \vec{k}_0) = \vartheta$ we have:

$$k_\varrho^2 = |\tfrac{1}{2}(\vec{k}_n - \vec{k}_p)|^2 = \tfrac{1}{4}(k_n^2 + k_p^2 - 2k_n k_p\cos\theta), \tag{15}$$

$$s^2 = |\vec{k}_0 - \vec{k}|^2 = k_0 + k_n^2 + k_\varrho^2 - 2k_0 k_n\cos\vartheta - 2k_0 k_p\cos(\theta-\vartheta) + 2k_n k_p\cos\theta, \tag{16}$$

$$(17)\quad |\vec{k}\times\vec{k}_0|^2 = k_0^2(k_n^2\sin^2\vartheta + k_p^2\sin^2(\theta-\vartheta) + 2k_nk_p(\cos\theta - \cos(\theta-\vartheta)\cos\vartheta)),$$

$$(18)\quad \cos\gamma = \frac{1}{2k_\varrho s}(k_0k_n\cos\vartheta - k_0k_p\cos(\theta-\vartheta) + k_p^2 - k_n^2).$$

At first, we note that P is independent of Z. For $Ze^2/\hbar v_0 \rangle, 1$, it is necessary to calculate with the exact Coulomb wave functions, and then P would depend on Z in terms of the Gamow parameter n_d. If we had no singlet state final $n-p$ interaction ($a_0 \to -\infty$), P would be zero, in the same way as P for the $D(\gamma, n)$ reaction ([8]–[9]). The denominator of P – (14) gives the angular distribution which should itself be investigated experimentally. If $|\cos\gamma| \sim 1$, the magnetic (second) term in the denominator is, for $E_0 \sim 100-200$ MeV, smaller by one or two orders of magnitude than the electric (first) term. The situation is reversed if $\cos\gamma \ll 1$, $s \to 0$. Large polarization occurs, in general, at very small $\cos\gamma$ and P is very sensitive to both the angles θ and ϑ for k_0 and k_n fixed. As in the case of $P(\theta_{\text{scatt}})$, for the magnetic scattering of neutrons from nuclei [10] P increases with the increase of E_0 at k_n/k_0, θ and ϑ being fixed. P vanishes if: 1) $\vec{k}_n = \pm\vec{k}_p$, i. e., $k_n = k_p$, $\theta = 0, \pi$; 2) $\vec{k} \uparrow\uparrow \vec{k}_0$ or $\vec{k} \uparrow\downarrow \vec{k}_0$; 3) $\cos\gamma = 0$. If $k_n \cong k_p$, P is zero for $\cos\vartheta = \cos(\theta-\vartheta)$, e. g., $\theta = 2\vartheta$. The sign of the polarization is

$$(19)\quad \operatorname{sgn} P = \operatorname{sgn}\cos\gamma = \operatorname{sgn}\left\{\sqrt{2}\left(\sqrt{\frac{E_n}{E_0}}\cos\vartheta - \sqrt{1-\frac{\epsilon}{E_0}-\frac{E_n}{E_0}}\cos(\theta-\vartheta)\right) + 1 - \frac{\epsilon}{E_0} - \frac{2E_n}{E_0}\right\}.$$

If $E_n \cong E_0/2$ and $\epsilon/E \ll 1$, then $\operatorname{sgn} P = \operatorname{sgn}(\cos\vartheta - \cos(\theta-\vartheta))$. E. g., if $\theta \ll 1$, then $\operatorname{sgn} P = \operatorname{sgn}\sin\vartheta$ and $P > 0$ for $0 < \vartheta \leqslant \pi$. The simplest example on the basis of which to interpret (14) is the case $E_n \cong E_p \cong E_0/2$. Then: $k_\varrho = (k_0/2)\cdot\left|\sin\frac{\theta}{2}\right|$,

$$s = k_0\sqrt{3/2 - \cos\vartheta - \cos(\theta-\vartheta) + 1/2\cos\theta},\ |\vec{k}\times\vec{k}_0| =$$

$$= (1/2)k_0^2 \times \sqrt{\sin^2\vartheta + \sin^2(\theta-\vartheta) + 2(\cos\theta - \cos(\theta-\vartheta)\cos\vartheta)}$$

$$\cos\gamma = \frac{k_0^2}{4k_\varrho s}(\cos\vartheta - \cos(\theta-\vartheta)).$$

Already at $E_0 = 100$ MeV, $\vartheta = 10°$, $\theta = 18°$ we get $P = -21.5$ per cent. P of about the same magnitude, and greater, appear at larger angles.

If we did not use the neutron-proton coincidence method, but simply neutrons, of, say, energy E_n and angle ϑ at a given E_0, we should have to integrate over θ. In this integration (by numerical methods), the region of θ corresponding to the impact parameters for which the nuclear

interactions would be important, should be eliminated (see, e. g., [1], [3], [5]). These values of θ corresponding to $s > s_{\max} \sim 1/R_0$, where $R = R$ (nucleus) $+ R$ (deuteron). This procedure is, however, somewhat crude, especially for the magnetic terms. The more exact calculation would be very cumbersome and the labour involved is not justified at present. The same applies to the generalization for the case of non-central $n-p$ forces. For higher energies, the relativistic corrections of higher order indicated by Rosenzweig and Sitenko [6], should be taken into account.

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EXPERIMENTAL PHYSICS

Anisotropic Small-Angle Scattering of X-rays in Graphite

by

J. AULEYTNER and M. LEFELD

Presented by A. SOŁTAN on December 7, 1956

Natural (Ceylon) powdered graphite pressed into narrow capillaries shows a strong orientation. The crystallites are arranged about the direction of the pressing in the following manner: the normals to the 002 plane point in this direction or deviate from it by a small angle. This may be shown by irradiating a thin beam of X-rays perpendicular to the axis of the cylinder with the appropriately prepared sample. The Debey-Scherrer rings having indices 002 and 100 are then observed to be strongly darkened in directions perpendicular to one other (Fig. 1). Such a phenomenon suggests that the small-angle scattering of X-rays in graphite also has an anisotropic character. This would indicate the appearance in the sample of ordered regions differing as regards electronic density. Making use of this phenomenon, we can determine the size of these heterogeneities and obtain some information regarding their shape. Debey-Scherrer photographs were obtained by means of a fine focus tube with a circular focus of 25 μ diameter constructed by the author.

In the investigations of small-angle scattering the camera used was designed on the principle given by Kratky [1] (Fig. 2).

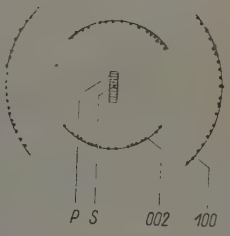

Fig. 1

The collimating arrangement has an additional slit S_2, which was needed both to facilitate the determination of the collimating correction and to avoid parasitic scattering. A monchromatized beam of X-rays of wavelength $\lambda_{KaFe}=1.93$ Å was employed. The anode current was 7 mA and anode voltage 30 kV. The time of irradiation with a sample-to-photographic-plate distance of 130 mm. was 14 hours. Photographs of 180 mm. were also obtained.

The sample was in the shape of a rod of 0.5 mm. diameter, so arranged that the incident beam was perpendicular to its axis.

Two photographs were made under the same experimental conditions; the first with the collimater slit lying in the plane perpendicular to the sample axis, and the second parallel to the axis of the sample.

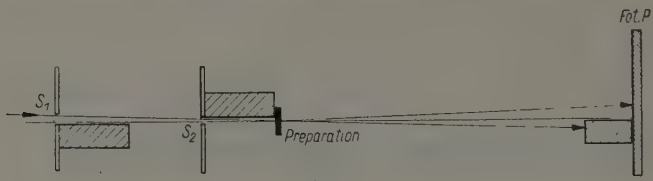

Fig. 2

In the first case, the angular region embraced by the recorded scattering was much greater than in the second (Figs. 3, 4, 5). When the sample was irradiated in the direction of the pressing, the angular region of scattering was considerably smaller than in cases I and II.

Fig 3. Fig. 4

On the basis of the relations given by Guinier [2] for oriented regions $F^2(h)=F^2(0)\exp(-h^2D^2(l_0))$ and using the tangential method, the dimensions of the scattering regions D in the direction l_0 were calculated. The vector l_0 denotes the direction normal to the plane of the grain diameter $\pi(l_0)$ and perpendicular to the photographic film (Fig. 6).

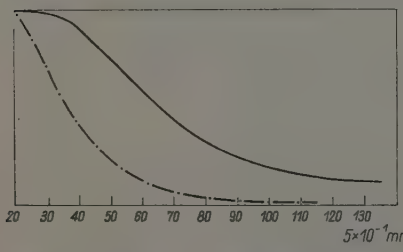

Fig. 5. Broken line corresponds to Fig. 3. Continuous liue corresponds to Fig. 4

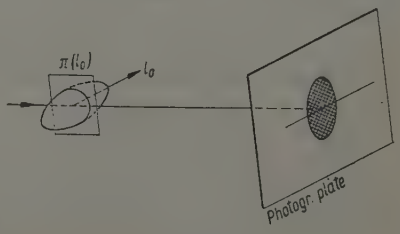

Fig. 6

The calculated values of D give the dimensions of the heterogeneities in directions perpendicular to one another.

The photographs of the interference pattern in the angular region from 5° to 45° with the use of polychromatic radiation shows considerable asterism, which is evidence of a strong deformation of the atomic lattice of the crystallites.

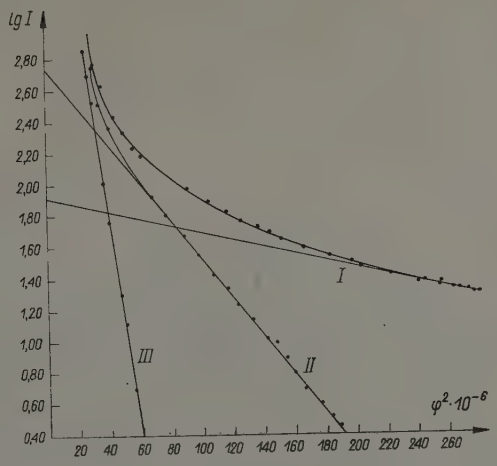

Fig. 7

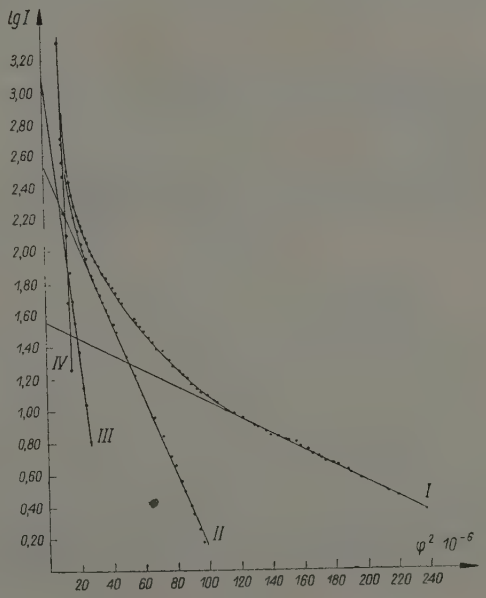

Fig. 8

The sizes determined for the regions responsible for small-angle scattering are considerably smaller than the size of the graphite crystallites contained in the sample. The size of the crystallites is of the order of 10^{-4} and 10^{-5}cm., and the size of the regions distinguishable as regards the electronic density is 10^{-6} and 10^{-7} cm. These regions are oriented in the same direction as the crystallites. It may therefore be supposed

TABLE I

	D_I(Å)	%	D_{II}(Å)	%	D_{III}(Å)	%	D_{IV}(Å)	%
Slit lying in a plane perpendicular to the axis of the sample	22	22	51	12	123	66	—	—
Slit parallel to the axis of the sample	32	0.3	71	0.3	135	0.1	272	99.3

that the occurrence of anisotropic small-angle scattering of X-rays is the result of the existence of big gaps in the atomic lattice of the crystals.

The lattice deformation causing the observed asterism is surely connected with the existence of gaps in the graphite crystals. Calculations of the size of the heterogeneities were made for samples in which the maximum deviation of the normal to the 002 plane from the longitudinal axis of the sample was 35°. The maximum error resulting from the inaccuracy of the measurement was 5%.

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EXPERIMENTAL PHYSICS

Estimation of the Potential Barrier Height of Torsional Rotation in CH_3SH Molecules by Means of Slow-Neutron Scattering

by

A. BUDZANOWSKI, K. GROTOWSKI, J. A. JANIK,
F. MANIAWSKI, H. RŻANY, A. SZKATUŁA, A. WANIC

Presented by H. NIEWODNICZAŃSKI on December 1, 1956

In previous papers by one of the authors [1], [2] experimental investigation of the influence of the torsional rotation effect in the CH_3OH molecule on the scattering of slow neutrons was considered. The results obtained in the above-mentioned papers were interpreted as being in accord with the theory of the influence of torsional rotation on the scattering of neutrons as given by Kołos [3].

Because of the difficulty in arriving at a correct interpretation of the results in the case of liquid CH_3OH, this difficulty being connected with the strong association of the alcohol molecule, an analogous investigation was carried out for molecules of methyl mercaptan. There was a large divergence among the data given by different sources [4]—[7] as regards the height of the potential barrier of torsional rotation for the CH_3SH molecule. Thus it would serve no purpose to investigate the agreement with the theory of Kołos of the results obtained. It seems, however, that it would be interesting to use the measured values of the cross-section for neutron scattering in CH_3SH and, by means of Kołos' theory, to estimate the potential barrier height for torsional rotation in this molecule.

The measurements were made by means of a Ra + Be neutron source containing 100 mg. of radium. Thermal neutrons were obtained by means of the slowing down of neutrons in paraffin wax moulded in the shape of a neutron "gun". As a neutron detector, a multi-plate, argon filled ionization chamber with boron-coated electrodes was employed. The chamber worked together with an amplifier, pulse discriminator, and counter [8]. The scatterer consisted of liquid CH_3SH placed in a flat-walled brass vessel.

The relative cross-section measurements were made by using water as the reference substance with a known cross-section of 91 barns for thermal neutrons [9].

The cross-section obtained in these experiments for thermal neutron scattering by CH_3SH molecular is

$$\sigma_{CH_3SH} = (194.1 \pm 5) \text{ barns.}$$

Before going on the estimate the potential barrier height of torsional rotation in CH_3SH molecules (which may be done on the basis of the above result), we should analyse the present state of knowledge of this barrier (V_0). Calculations on the basis of thermodynamic data for CH_3SH give us for V_0 the value 1460 cal./mole [4]. From the data obtained by means of microwave spectroscopy the barrier heights calculated by various authors are as fóllows: (1060 ± 120) cal./mole [5], (800 ± 140) cal./mole [6], (705 ± 45) cal./mole [7]. The last value was obtained by Kilb in 1955.

Taking this last value, Kołos calculated the theoretical value of the ratio $\sigma_{CH_3SH}/\sigma_{rig}$ as a function of the neutron energy [10]. σ_{rig} denotes the cross-section for neutron scattering by rigid molecules and can be calculated from the theory given by Sachs and Teller [11], for CH_3SH, σ_{rig} is 258 barns. For an energy of 0.037 eV, $\sigma_{CH_3SH}/\sigma_{rig} = 0.70$ or $\sigma_{CH_3SH} = 181$ barns.

This value lies a little below the lower limit of the error of the value obtained experimentally.

The following alternatives seem to provide the correct interpretation of this discrepancy:

1. V_0 is approximately equal to the value given by Kilb (705 cal./mole) and the discrepancy obtained arises from the fact that Kołos did not take into account the influence of inelastic scattering of neutrons due to torsional rotation.

2. V_0 is greater than Kilb's value, in which case inelastic scattering cannot in general arise or does not play any important role.

The approximate estimation of V_0 in case 2 based on Kołos' calculations for CH_3OH, which are similar to those for CH_3SH, and on the values of σ_{CH_3SH}, as measured in the experiments described here, results in a barrier height of about 1000 cal./mole.

The values we obtained for the cross-section of neutron scattering by CH_3SH molecules permit us to estimate the potential barrier height in these molecules as being about 700 cal./mole or about 1000 cal./mole; the value of 1460 cal./mole obtained from the thermodynamic data does not enter into account.

We wish to express our thanks to Professor H. Niewodniczański for discussions during the experimental work, to Mrs J. Janik for preparing the required amount of CH_3SH, to Mrs. R. Michalska for her cal-

culations concerning the relative measurements of the cross-sections, to Mrs. W. Szymczyk and to the members of the Students Physics Club of the Jagellonian University for carrying out auxiliary measurements.

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EXPERIMENTAL PHYSICS

Hyperfine Structure of the Forbidden Cd I Line λ 3141 Å. U. ($5s^2\ ^1S_0 - 5s\ 5p\ ^3P_2^0$)

by

F. LEŚ and H. NIEWODNICZAŃSKI

Presented by H. NIEWODNICZAŃSKI on January 7, 1957

The nature of forbidden spectral lines was investigated in a number of theoretical and experimental works [1], [2], [8]. It was then determined that certain lines, forbidden for spontaneous electric dipole radiation, are allowed for magnetic dipole radiation and for electric quadrupole radiation. There exists, however, a class of forbidden lines which are strictly forbidden for both spontaneous electric radiation and spontaneous magnetic radiation of any polarity. According to Bowen's hypothesis some spectral lines of this kind may come from the electric dipole radiation arising by the interaction between the magnetic moment of the nucleus of an atom and the electrons of its shell. Hence, the transitions between the energy levels, corresponding to these lines, may take place only in atoms in which the magnetic moment of the nucleus differs from zero. To this class of forbidden lines belong the intercombination lines in the Hg I spectrum: λ 2270 Å. U. ($6s^2\ ^1S_0 - 6s6p\ ^3P_2^0$), λ 2656 Å.U. ($6s^2\ ^1S_0 - 6s6p\ ^3P_0^0$) and λ 2967.5 Å. U. ($6s6p\ ^3P_0^0 - 6s6d\ ^1D_2$), and in the Cd I spectrum the lines, λ 3320 Å. U. ($5s^2\ ^1S_0 - 5s5p\ ^3P_0^0$) and λ 3141 Å. U. ($5s^2\ ^1S_0 - 5s5p\ ^3P_2^0$). All these lines correspond to the forbidden even-odd transitions with $\Delta J = 2$ or $J = 0 \rightarrow J = 0$. In both elements only odd isotopes have spins different from zero, hence only odd isotopes of mercury and cadmium may emit such lines. Direct proof of this hypothesis can be obtained by an analysis of the isotopic hyperfine structure of the investigated line in which only those components of the line will appear which correspond to odd isotopes.

A detailed analysis of the isotopic structure of optically excited forbidden Hg I lines λ 2656 Å. U., λ 2270 Å. U. and λ 2967.5 Å. U. carried out by Mrozowski [6], [7] completely confirmed Bowen's hypothesis in respect to mercury. In fact, these lines are emitted only by isotopes

of mercury having mass numbers 199 and 201 and spins 1/2 and 3/2. In this case the intensity of respective groups of hyperfine structure components is proportional to the content of odd isotopes.

The analogous forbidden intercombination Cd I lines λ 3141 Å. U. and λ 3320 Å. U., found by Foote, Takamine and Chenault [4], are weaker than those emitted by mercury, owing to the more strictly valid intercombination forbiddeness and the smaller abundance in natural cadmium of odd isotopes ^{111}Cd and ^{113}Cd. The nature of these forbidden cadmium lines was investigated by Holmes and Deloume [5]. Having compared the intensities of the forbidden line λ 3141 Å. U. emitted by natural cadmium and also by a sample of cadmium enriched in one of odd isotopes having mass number 111, they found that, at the same excitation conditions (high frequency discharges), the intensity of this line increased linearly with the increase of the relative content of this isotope. This is an indirect indication that the examined line is emitted only by the odd isotopes of cadmium. In this investigation exact intensity measurements were, however, rendered impossible owing to the close neighbourhood of other strong cadmium lines.

The aim of the present investigation was to find a more direct proof of the validity of Bowen's hypothesis in respect to the forbidden Cd I lines by investigation of the isotopic structure of the line λ 3141 Å. U. ($5s^2\,{}^1S_0 - 5s5p\,{}^3P_2^0$). It is known that the isotope shift for Cd I spectral lines

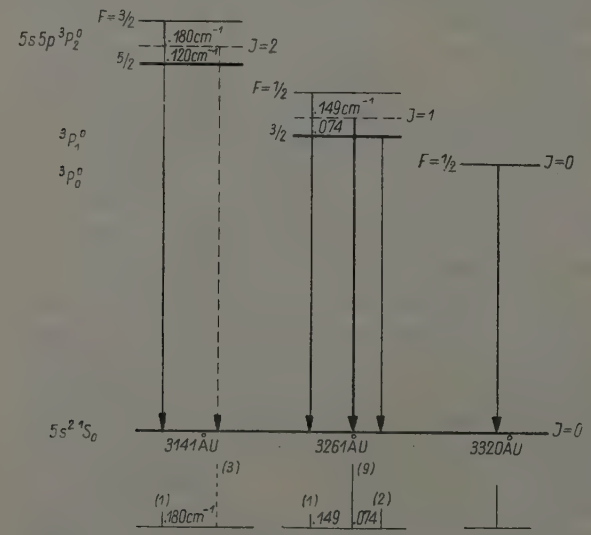

Fig. 1. The splitting of energy levels for the $5s^2\,{}^1S_0 - 5s5p\,{}^3P_{2,1,0}^0$ multiplet in the Cd I and its hyperfine structure. Dashed horizontal lines indicate common energy levels of even isotopes

is extremely small [3]. Therefore in our work we were compelled to utilise only the splitting of energy levels of odd isotopes caused by their nuclear spins. It can be seen from the diagram of the hyperfine structure levels of the multiplet $5s^2\ {}^1S_0 - 5s5p\ {}^3P^0_{2,1,0}$ (Fig. 1) that only the line λ 3141 Å. U. is suitable for measuring. Two odd isotopes ^{111}Cd and ^{113}Cd existing in the natural isotopic composition have equal spins 1/2, hence the corresponding hyperfine structure levels of both isotopes coincide. If, therefore, the hypothesis concerning the enforcement of the line λ 3141 Å. U. by the nuclear magnetic moment is not right, and this line is emitted by all cadmium isotopes, then it should be composed of two fringes lying at a distance of 0.180 cm.$^{-1}$ from each other. This distance was measured by Schüller and Keystone [10] who analysed the hyperfine structure of the cadmium line λ 5086 Å. U. ($5s5p\ {}^3P^0_2 - 5s6s\ {}^3S_1$). The ratio of intensities of the two components of the line λ 3141 Å. U. is then expected to be the same as the ratio of the content of even isotopes to that of odd ones. The isotopic structure of natural cadmium is as follows:

even isotopes		odd isotopes	
Cd 106 —	1.22 per cent	Cd 111 —	12.78 per cent
108 —	0.97 „ „	113 —	12.30 „ „
110 —	12.35 „ „		25.08 „ „
112 —	24.00 „ „		
114 —	28.75 „ „		
116 —	7.63 „ „		
	74.92 „ „		

It can be seen from the above that the relative content ratio of even and odd isotopes is almost exactly equal to 3 : 1. If, however, Bowen's hypothesis is correct, then the fringe representing the even isotopes in the hyperfine structure of the line λ 3141 Å. U. will not appear and this line will be reduced to a single fringe.

In order to obtain the answer as to which of these possibilities is true, the hyperfine structure of the forbidden cadmium line λ 3141 Å. U. was experimentally examined by the authors. For this purpose it was necessary to construct a source of light which would emit this line with a sufficiently high intensity. The intensity of the forbidden line λ 3141 Å. U. emitted by light sources with electrodeless discharges, as applied in former investigations, was too small for the hyperfine structure analysis. The authors have constructed and applied different kinds of light sources using high frequency electrodeless discharges but the intensity of the forbidden line λ 3141 Å. U. still remained insufficient. In the course of further experiments it became evident that better results were obtained by application of a Schüler-type lamp with hollow cathode. Such a lamp, of a similar shape to that designed by Ritschl [9], after being thoroughly evacuated and degassed, was filled with spectro-

scopically pure helium up to a pressure of several mm. Hg. The cathode, made of brass, was provided with an insert of cadmium having 4 mm. inside diameter and about 40 mm. in length. When a current of 120 mA was applied, the line λ 3141 Å. U. appeared distinctly in exposures not exceeding 5 minutes. Fig. 2 represents the microphotometric curve of the spectrum obtained by means of a small Zeiss quartz spectrograph on an "Ultrapan Super" photographic plate produced by Film Polski in an exposure lasting about 15 minutes. Further extension of the exposure time was found to serve no purpose owing to the appearance of the background produced by strong wings of the λ 3261 Å. U. cadmium resonance line.

As an instrument of high resolving power a Fabry-Perot interferometer was used which was crossed with a medium size quartz spectro-

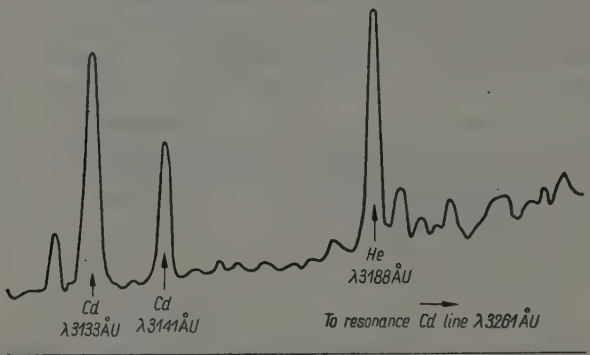

Fig. 2. Microphotometer record of the part of the spectrum containing the forbidden line λ 3141 Å. U.; the background is due to the strongly overexposed Cd resonance line λ 3261 Å. U.

graph of very high luminosity. The interferometer consisted of plane-parallel plates of fused silica covered on both sides with semi-reflecting layers of aluminium. The thicknesses of the mirror coatings, and hence their transparencies were experimentally adjusted so as to reduce the time of exposure to several hours; the reflecting powers were at the same time high enough to assure satisfactory resolving power of the interferometer. The interferential image was projected on the slit of the quartz spectrograph by means of a quartz-fluorite achromatic compound lens having a focal distance of 250 mm. When the optical thickness of the interferometer plate was 10 mm. the dispersion range amounted to 0.500 $cm.^{-1}$, hence the fringes lying 0.180 $cm.^{-1}$ apart should have been easily resolved. The resolving power and the dispersion range were verified by an analysis of the well known hyperfine structure of the resonance cadmium line λ 3261 Å. U. It can be seen from the microphoto-

metric curve of the interference image of the line λ 3141 Å. U. that it is composed of one fringe only (Fig. 3). The height corresponding to the intensity of the second fringe, which would appear if line λ 3141 Å. U. were emitted by the even as well as by the odd cadmium isotopes, was estimated on the basis of the blackening curve of the photographic plates being used (Fig. 4). It can be seen in this figure that should one ascribe the fringe obtained in the experiment to the even isotopes, then a corresponding weaker fringe representing the odd isotopes would certainly

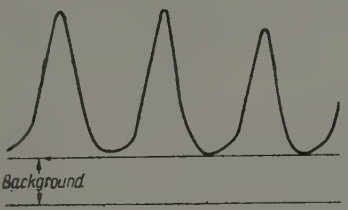

Fig. 3. Microphotometer record of the hyperfine structure of the forbidden Cd I line λ 3141 Å. U.

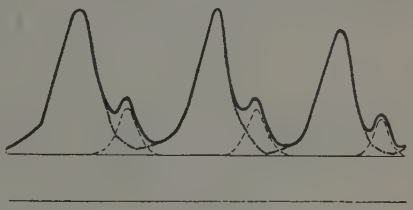

Fig. 4. · — · — · — Microphotometer curve as in Fig. 3.
— — — — the supposed (calculated) second component.
——— the resultant expected blackening curve.

be observed. Lack of this fringe in the observed structure of the forbidden line is a proof that this line is emitted only by one kind (either even or odd) of cadmium isotopes. As there is no reason to suppose that the observed single fringe appearing in the hyperfine structure of the forbidden cadmium line λ 3141 Å. U. is emitted only by the even isotopes, the conclusion must be drawn that this line in accordance with Bowen's hypothesis is emitted solely by two odd cadmium isotopes having mass numbers 111 and 113.

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CHEMISTRY

Vapour-Liquid Equilibria. I. An Apparatus for Determining the Vapour-Liquid Phase Equilibria

by

W. ŚWIĘTOSŁAWSKI, K. ZIĘBORAK and W. BRZOSTOWSKI

Presented by W. ŚWIĘTOSŁAWSKI on November 3, 1956

Introductory remarks

The vapour-liquid equilibrium investigations are important in studying the distillation and rectification processes. There are large numbers of different devices, working on different principles, used for these investigations. The ones most frequently used and giving the best results are those which involve recirculation of vapour condensate through the boiling liquid. The recently most widely adopted apparatus are those used by Othmer [1]—[4] and Gillespie [6]. The disadvantage of the Othmer device consists in the condensation of small amounts of vapour in the upper portion of the apparatus. The heating jacket, used by Othmer in his modified apparatus, may, in spite of the fact that the external temperature is lower than that measured inside the apparatus, exert some influence on the equilibrium. In Gillespie's apparatus, the cold condensate is recycled. The recycled distillate has a lower boiling point, and flash vaporisation may occur, somewhat disturbing the equilibrium. Moreover, according to Katz and Newman [7], the density of the cold distillate may be greater than that of the residual liquid; this may lead to stratification and to the formation of vapour which is in equilibrium with the liquid found only in the top stratum.

Bushmakin and Voeikova [8], [9] carried out investigations using a number of different apparatus. They described their own apparatus, modified recently by Bushmakin. According to Bushmakin's observations, most of the vapour-liquid equilibrium devices give sufficiently exact data, but they must operate at optimal conditions, adjusted each time to specific details in construction and dimensions. Moreover, these conditions depend upon the object under investigation and therefore use up time in the preliminary examination. Bushmakin's own apparatus does not

need such investigations and may be considered as one of the best in operation.

Fowler and Lim [10] described the results of their investigations on the benzene-carbon tetrachloride system using the Fowler and Morris [11] device. The system investigated by Fowler and Lim was previously examined by 12 authors, who obtained different results. On the other hand, the Fowler and Lim results agree well with those obtained by Bushmakin and Voeikova.

The common disadvantage of all the apparatus hitherto used consisted in the fact that no exact boiling temperature of the mixtures could be measured. In some of them (e. g., Bushmakin), it cannot be measured at all; in others (e. g., Othmer), the accuracy of the boiling temperature determination is insufficient. Some of the investigators, wanting to have the complete set of x,y,t data, made two parallel series of measurements; one consisted in the determination of x,y data and the other in measuring the boiling temperatures by means of Świętosławski's ebulliometer. The latter was mentioned by Bushmakin, as well as by other authors. We attempted to solve the problem of simultaneous determinations of x,y and t by modifying the ebulliometer for this specific purpose.

The apparatus

The simple, one-stage ebulliometer, described by one of us [12] was modified as shown in Fig. 1.

In a modified ebulliometer, the liquid is brought — as usual in such types of apparatus — to boiling in A. The vapour carries the boiling liquid and throws it on to the surface of the well W, where the boiling temperature is measured. The vapour then passes through D to the condenser. In order to avoid the entrainment of liquid by the vapour to the condenser, D is used instead of the usual horizontal tube which leads to the condenser. The condensate flows down through the drop-counter F to the vapour trap V. The excess of the condensate returns through E into B, where it is immediately mixed with the liquid flowing down along the external surface of the well W. After half an hour of this operation, the equilibrium throughout the system becomes stabilised, and samples from B and V can be taken by means of the two stopcocks K_1 and K_2. The receiver for the samples is illustrated in Fig. 2.

Testing the device

Tests as to the proper functioning of the apparatus were carried out in two ways. The first was the method used by one of us for examining liquids containing small amounts of a highly volatile compo-

nent [13]. The advantage of the use of such an apparatus consisted in the possibility of the almost complete elimination of the influence of the dead space. In fact, as mentioned in § 9 of *Ebulliometric measurements*, the elimination of the error caused by the presence of the dead space consists in carrying out two and, if necessary, three consecutive experiments. The first of these is the vapour-liquid equilibrium determination, as mentioned above, without removal of the liquid found in V (Fig. 1) obtained as a result of the vapour condensation. After equilibrium is reached as between the compositions in the container and in the vapour trap, the liquid contained in A and in B is removed by means of the stopcock K_1. Then the ebulliometer is filled with a new portion of the starting liquid. The procedure may be repeated several times until no changes in the compositions of the samples taken from B and V are obtained.

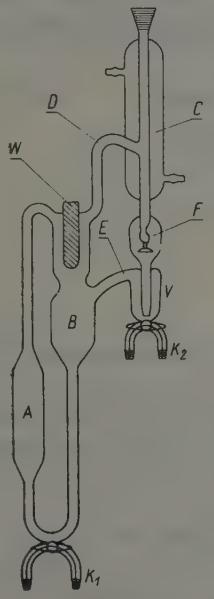

Fig. 1. Device for simultaneous measurements of vapour-liquid equilibrium and boiling temperature

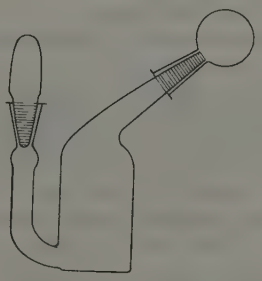

Fig. 2. The sample receiver

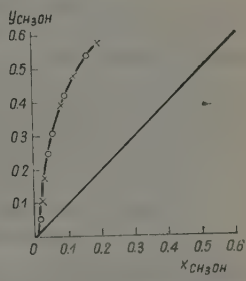

Fig. 3. Vapour-liquid equilibria for methanol-water system at 760 Torr
o — data obtained by us
× — Cornell's measurements

In the experiments made it sufficed to repeat the two operations just described for the total elimination of the influence of the dead space of the apparatus.

It must be emphasised that, when the mixture corresponded exactly to the composition of the azeotrope, no influence of the dead space was noted. On the contrary, the influence of the latter increased with the increase of the differences in composition of the liquids found in B and in V (Fig. 1).

We used another method also for the control of the proper functioning of the apparatus. That is, we repeated some of the experiments car-

ried out by Cornell and Montonna [14]. The methanol-water system was used in the region in which large differences in the compositions of the liquid and of the vapour phase took place. The comparison of the results is shown in Fig. 3.

Summary

A one-stage ebulliometer adjusted for vapour-liquid phase equilibrium determinations is described. A method used for eliminating the influence of the dead space similar to that described in the *Ebulliometric measurements* gave satisfactory results.

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CHEMISTRY

Vapour-Liquid Equilibria. II. The *n*-Decane-Acetic Acid-2,6-Lutidine System

by

K. ZIĘBORAK and W. BRZOSTOWSKI

Presented by W. ŚWIĘTOSŁAWSKI on November 3, 1956

Introductory remarks

The system under consideration was previously investigated by one of us by the ebulliometric method [1] and was found to form a positive-negative azeotrope. The method used in those, as well as in other investigations [2]—[4], was described by Świętosławski [5]. Subsequently, a number of ternary positive-negative systems was examined, which, however, in only a few instances enabled the vapour-liquid equilibria to be determined. The first to be investigated was the chloroform-acetone-methanol system (by Lang [6]).

The purpose of this paper was to establish the vapour-liquid equilibria for a positive-negative ternary system composed of a weak acid, a weak base and a paraffin. The *n*-decane-acetic acid-2,6-lutidine system was chosen because of its peculiar properties [1].

Experimental part

The apparatus used in the present investigations has been described in the preceding paper [7].

The system under investigation was partially immiscible at room temperature. The preliminary experiments consisted in determining the solubility line of the system. This was done by the preparation of a binary mixture of known composition and by successive additions of small amounts of the third component in isothermal conditions. The quantity of each of the components was determined by weighing, and the turbidity points were determined in a conventional way. The results obtained are presented in Table I and in Fig. 1.

Analytical methods

Potentiometric titrations of ternary mixtures of different compositions were made. The titration of acetic acid, in the presence of 2,6-lutidine, with potassium hydroxyde gave satisfactory results, the sharp change of the titration curve in the range pH 8—10 being readily observed. In this range of pH, tymolphtalein was found to be the best indicator.

TABLE I

The mutual solubility data of the ternary system at 25°C.

No.	Composition in percentage weights		
	A	*P*	*H*
1	22.6	36.6	40.8
2	26.1	44.5	29.4
3	40.4	46.8	12.8
4	68.0	29.1	2.9
5	17.5	0.0	82.5
6	91.2	0.0	8.8
7	6.8	19.8	73.4
8	11.4	27.9	60.7

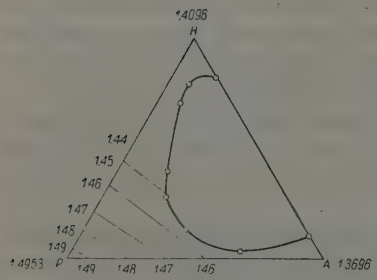

Fig. 1. Mutual solubility curve and refractive indices at 25°C. of the acetic acid (*A*) — 2,6-lutidine (*P*) — *n*-decane (*H*) system
Compositions expressed in weight percents

The remaining components were determined by the indirect method, that is by measuring at 25°C. the refractive indices of the binary and ternary mixtures. A Zeiss refractometer, of the Abbé type, linked with a Höppler ultrathermostate was used. The lines of constant refractive indices in the ternary system are presented in Fig. 1.

Binary systems

The results of examination of the vapour-liquid equilibria of the binary mixtures are presented in Table II, and in Figs. 2, 3 and 4.

Ternary system

In the same manner were examined the vapour-liquid equilibria of the ternary system. The results obtained are given in Table III and the connodes are presented in Fig. 5, including the top-ridge and valley lines [4].

TABLE II

Vapour-liquid equilibria in binary system
The 2,6-lutidine — *n*-decane system

Run No.	Boiling temperature	Mole fraction of 2,6-lutidine	
		x_p	y_p
1	174.00	0.000	0.000
2	162.43	0.178	0.392
3	159.80	0.232	0.487
4	157.25	0.322	0.572
5	151.82	0.502	0.723
6	149.48	0.609	0.788
7	147.85	0.706	0.831
8	147.82	0.709	0.835
9	145.23	0.886	0.940
10	143.41	1.000	1.000

The acetic acid — 2,6-lutidine system

		Mole fraction of acetic acid	
		x_A	y_A
1	143.41	0.000	0.000
2	144.92	0.075	0.035
3	145.83	0.138	0.095
4	147.15	0.284	0.258
5	147.28	0.352	0.360
6	147.01	0.416	0.440
7	146.60	0.471	0.536
8	144.67	0.605	0.748
9	144.60	0.621	0.785
10	141.36	0.748	0.918
11	130.46	0.887	0.991
12	127.43	0.911	0.999
13	118.04	1.000	1.000

The acetic acid — *n*-decane system

		Mole fraction of acetic acid	
		x_A	y_A
1	118.04	1.000	1.000
2	117.17	0.994	0.982
3	116.50	0.988	0.969
4	116.19	0.975	0.955
5	116.10	0.969	0.949
6	116.13	0.919	0.930
7	116.13	0.917	0.929
8	116.14	0.897	0.927
9	116.43	0.821	0.913
10	116.51	0.762	0.915
11	116.71	0.690	0.913

TABLE III

Vapour-liquid equilibria in the ternary system

Run No.	Boiling temperature	Liquid composition			Vapour composition		
		x_A	x_P	x_H	y_A	y_P	y_H
1	148.02	0.072	0.554	0.373	0.113	0.662	0.225
2	145.95	0.037	0.683	0.280	0.036	0.797	0.167
3	146.31	0.137	0.612	0.251	0.172	0.648	0.180
4	143.96	0.213	0.560	0.227	0.290	0.520	0.189
5	143.53	0.073	0.776	0.150	0.059	0.829	0.111
6	144.20	0.124	0.730	0.146	0.111	0.771	0.118
7	143.94	0.205	0.663	0.132	0.213	0.662	0.125
8	141.58	0.285	0.598	0.117	0.320	0.549	0.131
9	142.38	0.370	0.526	0.104	0.441	0.427	0.132
10	146.97	0.293	0.662	0.045	0.286	0.652	0.062
11	147.22	0.284	0.674	0.042	0.268	0.673	0.058
12	147.27	0.267	0.696	0.037	0.247	0.700	0.053
13	147.20	0.243	0.723	0.034	0.211	0.747	0.041
14	146.63	0.219	0.752	0.029	0.180	0.786	0.034
15	146.22	0.199	0.774	0.027	0.156	0.813	0.030
16	146.11	0.188	0.787	0.025	0.143	0.829	0.027
17	146.40	0.204	0.695	0.101	0.198	0.701	0.101
18	146.48	0.203	0.697	0.099	0.194	0.705	0.101
19	146.32	0.194	0.710	0.096	0.185	0.719	0.096
20	146.44	0.179	0.733	0.088	0.159	0.754	0.085
21	146.79	0.245	0.657	0.097	0.251	0.641	0.108
22	146.18	0.284	0.625	0.090	0.305	0.589	0.106
23	146.02	0.316	0.597	0.087	0.360	0.532	0.107
24	145.62	0.371	0.549	0.080	0.431	0.460	0.108

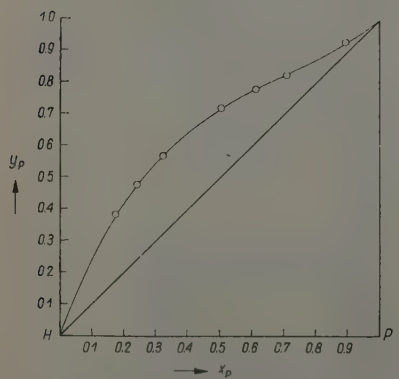

Fig. 2. Vapour-liquid equilibria for the 2,6-lutidine-*n*-decane system

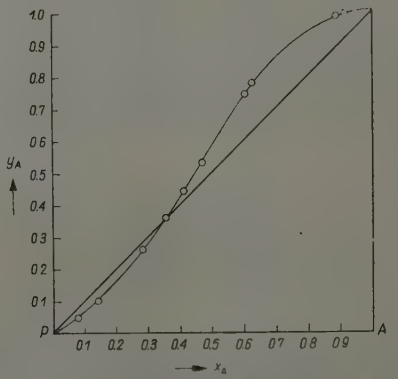

Fig. 3. Vapour-liquid equilibria for the acetic acid-2,6-lutidine system

Discussion of results

The compositions of the azeotropes and the course of the top-ridge line agree with those previously reported [1]. The course of the top-ridge and valley lines is marked by the shortest connodes (Fig. 5). The connodes become longer with the increase of the distance from the two characteristic lines mentioned above. The common direction of all the connodes on the top-ridge line is the saddle point *S*. On the valley line, the connodes have the opposite direction in relation to the saddle point. More detailed discussion of these results, with more detailed experimental data, will appear in Roczniki Chemii.

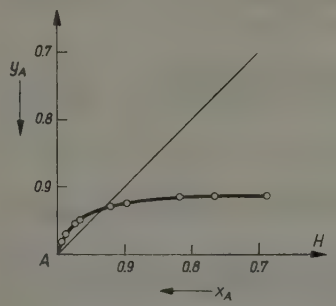

Fig. 4. Vapour-liquid equilibria for the acetic acid — *n*-decane system

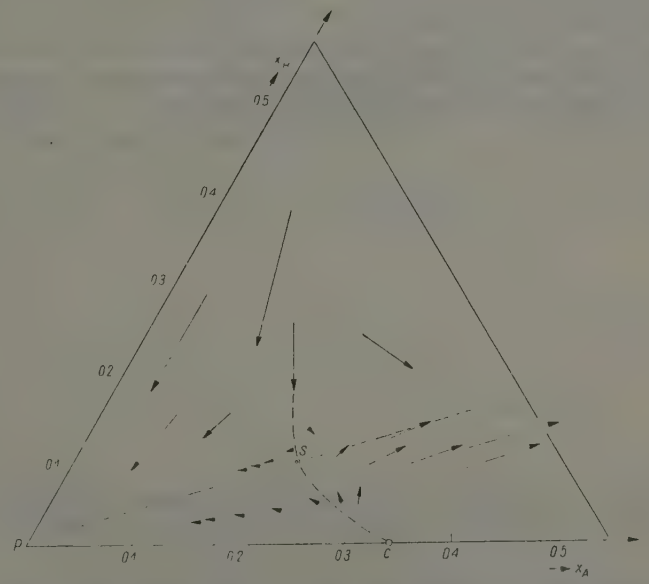

Fig. 5. The section of the concentration triangle for the ternary acetic acid (*A*) — 2,6-lutidine (*P*) — *n*-decane (*H*) system
Compositions expressed in molar fractions

We wish to express our best thanks to Professor W. Świętosławski for his help and suggestions.

Summary

1. The vapour-liquid equilibria in the ternary system formed by acetic acid 2.6-lutidine and *n*-decane were investigated.

2. The mutual solubility and the refractive index lines for the ternary system at 25°C. were determined.

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CHEMISTRY

On Endo- and Exoisomers of Nitroölefines (1-Cyclohexenyl- and Cyclohexylidenenitromethane). II

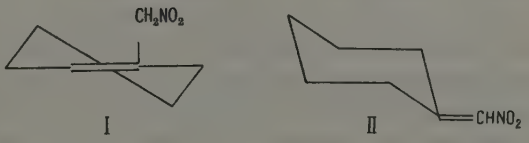
by

Z. ECKSTEIN, T. KRACZKIEWICZ, T. URBAŃSKI
and H. WOJNOWSKA

Presented by T. URBAŃSKI on December 10, 1956

In one of our former papers [1] we found that 1-cyclohexenylnitromethane cannot be prepared in a pure form by olefinisation of the acetyl derivative of 1-nitromethyl-1-hydroxycyclohexane. The product so obtained differed from 1-cyclohexenylnitromethane by its physical constants and some chemical reactions.

We originally suggested that one of the products of olefinisation would be an isomer of cyclohexenylnitromethane, i. e., cyclohexylidenenitromethane (II).



The product (I) is well known in the literature [2]—[5] and its structure can be expressed by the "half-chair" form of Barton [6]. The new product (II) which has now been obtained by us differed from the product (I). Thus, the ultraviolet absorption curve of the compound (I) did not show the maximum typical for the nitrogroup but only a slight bend in the region of 267—300 mμ and the new product (II) gave a sharp maximum at 262 mμ and the bend shifted to 312—350 mμ.

The difference between the absorption curves could be explained by the lack of conjugation of double bonds in the compound (I), where only two separate chromophores exist (*A*). On the contrary, the conjugation (*B*) exists in the compound (II).

Two separate chromophores of the type (*A*) do not suffice to create the maximum of the ultraviolet absorption curve, and this may be due to the steric influence on the nitrogroup of the cyclohexenyl ring. A similar effect has also been observed in the case of 1-cycloheptenylnitromethane [7] and of 1-nitromethyl-1-hydroxycyclohexane [8].

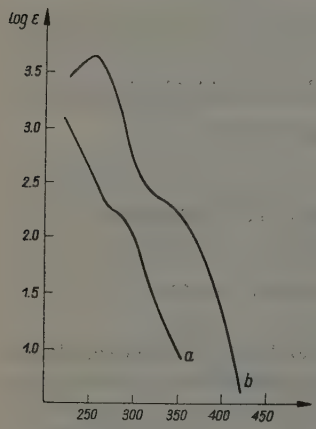
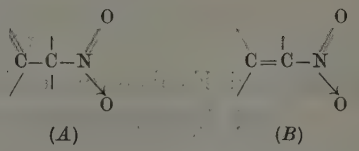


Fig. 1



(*A*) (*B*)

However, taking into consideration data existing in the literature, the formation of the isomer (II) should be regarded as not very probable. Some of the authors exclude the possibility of formation of the system $R=CHNO_2$, i. e., the existence of the structure with cyclohexylidenenitromethane group [9], [10]. This is based on the assumption of greater stability of the endocyclic (I), than of the exocyclic form (II) in cyclohexane and the tendency to transformation of the product (II) into (I).

The only argument in favour of the stability of the structure (II) would be the fact, that the active hydrogen attached to carbon with a nitrogroup always takes part in all known reactions of forming nitroölefines by splitting acetic acid off acetyl derivatives [3], [11]—[23].

In order to elucidate the problem of the structure of compound obtained by olefinisation of acetylated 1-nitromethyl-1-hydroxycyclohexane (with the probable structure (II)), its infra-red absorption spectrum was examined. To compare, the infra-red absorption of (I) was also investigated (Fig. 2, Table I).

The absorption curve of (I) is very similar to that of 1-cycloheptenylnitromethane according to experiments described in one of the former publications [7]. It shows the presence of characteristic vibrations of the double bond in cycloaliphatic rings ($\nu = 1666$ cm.$^{-1}$) and a marked shifting of deformation vibrations of CH_2 towards lower frequencies (1429 cm.$^{-1}$). Very prominent are both frequencies of the aliphatic nitrogroup (1555 and 1370 cm.$^{-1}$). Thus the structure of the compound (I) as 1-cyclohexenylnitromethane should be considered as being confirmed, although no clear maximum for NO_2 group can be found in the electronic spectrum (Fig. 1, Curve a).

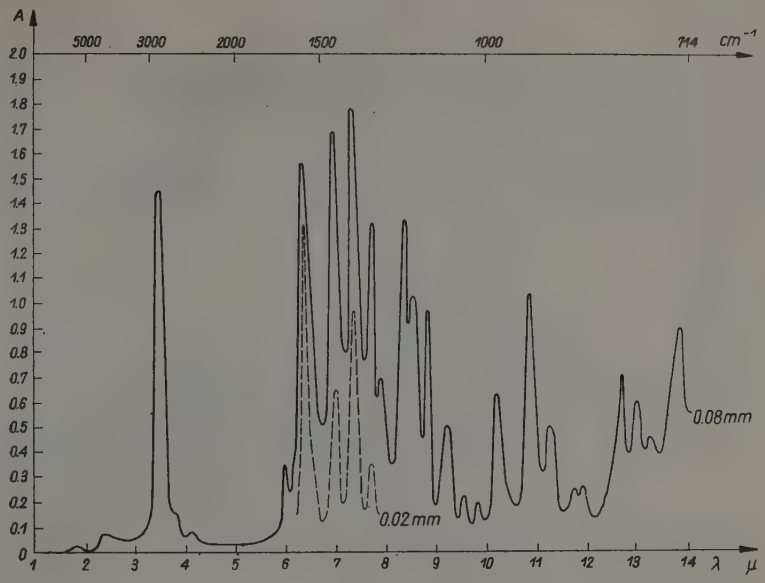


Fig. 2

The spectrum of the olefin (II) prepared from the acetylated 1-nitromethyl-1-hydroxycyclohexane is given in Fig. 3 and Table II.

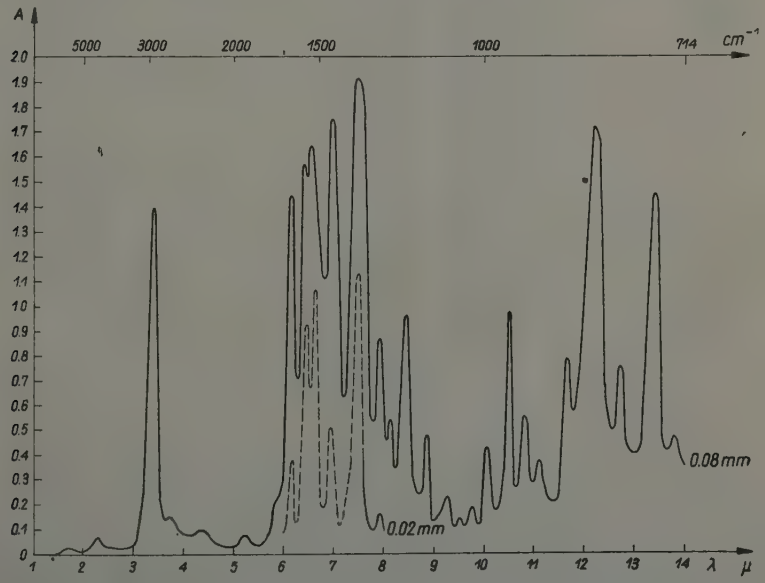


Fig. 3

TABLE I

Frequencies and absorption values for the maxima of the infra-red spectra of 1-cyclohexenylnitromethane (I) (width of the slot 0.08 mm.)

Wave numbers (cm.$^{-1}$)	$\log\frac{I^\circ}{I}$	Assignement
5555	0.0170	
4347	0.0641	
2898 (vs)	1.4559	
2666	0.1485	
2409	0.0820	
1666	0.3430	C=C in cycloaliphatic compounds
1555 (vs)	1.5528	NO_2 asym. stretching
1439 (vs)	1.6778	CH_2 deformation frequency in cycloaliphatic compounds, shifted under influence of the double bond C=C
1370 (vs)	1.7695	NO_2 sym. stretching
1306 (s)	1.3098	
1265	0.6904	
1197 (s)	1.3187	
1176 (m)	1.0132	
1136	0.9586	
1092	0.4922	
1047	0.2166	
1015	0.1869	
980	0.6090	
921	1.0270	
888	0.4829	
851	0.2161	
840	0.2519	
796	0.3526	
786	0.7011	
769	0.6037	
757	0.4510	
724	0.9031	

vs — very strong, s — strong, m — medium.

The absorption curve shows a characteristic splitting of the maximum of the nitrogroup (this is particularly prominent when the thickness of the layer is 0.02 mm.). In the region of 6μ two maxima can be seen: 1550 cm.$^{-1}$, typical for the nitrogroup [24], [25] and 1515 cm.$^{-1}$, which would correspond to the nitrogroup conjugated with the double

TABLE II

Frequencies and absorption values for the maxima of infra-red spectra of the mixture of nitroölefines (I) and (II)

Wave numbers ($cm.^{-1}$)	$\log\frac{I^\circ}{I}$	Width of the slot
5555	0.0119	
4347	0.0755	
2898 (vs)	1.4089	
2702	0.1428	
2300	0.1035	
1923	0.0712	0.08 mm.
1639	0.3747	
1550	0.9137	
1515	1.0864	
1449	0.5031	
1342	1.1249	
1265	0.1611	0.02 mm.
1694 (vw)	0.2103	
1626 (vs)	1.4319	
1576 (vs)	1.5528	
1526 (vs)	1.6383	
1439 (vs)	1.7448	
1351 (vs)	1.9586	
1265	0.8696	
1234	0.5497	
1190	0.9706	
1136	0.4842	
1081	0.2417	
1047 (vw)	0.1390	
1025	0.1965	
995	0.4283	
952	0.9829	
921	0.5591	
900	0.3799	
859	0.7932	
819	1.7212	
787	0.7569	
748	1.4559	
724	0.4737	0.08 mm.

vs — very strong, vw — very weak.

bond of methylene group (*B*). A similar shifting of frequency of the nitrogroup towards lower values has already been mentioned in the literature [10], [26].

It is known that the quantitative determination of isomeric nitroölefines in their mixture can be done by means of the infra-red absorption spectrum. Shechter and Shepherd [10] examined the mixture of 2-methyl-3-nitropropene and 2-methyl-1-nitropropene. They both possessed compounds in pure form and this simplified the quantitative analysis.

In our instance, only the isomer (I) was in the pure form, and the product obtained from the acetylated 1-nitromethyl-1-hydroxycyclohexane was a mixture of two isomers, (I) and (II). Therefore, it was impossible to use the ordinary methods of spectral analysis of mixture of two components.

The method described by Wright [27] allows to eliminate the influence of the presence of another substance on the band of the examined compound.

The curve (Fig. 4) shows the infra-red absorption of the mixture of isomers in solution in cyclohexane (2 ml. of the mixture were dissolved in 25 ml. of cyclohexane) in the range between 6.3 and 6.7 μ. Two bands have been obtained: the first with a wave length of 6.45 μ (frequency 1550 cm.$^{-1}$) corresponds to vibrations of the nitrogroup in the isomer (I), and the second, 6.575 μ (frequency 1519 cm.$^{-1}$), would be assigned to the nitrogroup conjugated with a double bond in the isomer (II). The influence on the 6.45 μ band of isomer (II) was eliminated by plotting

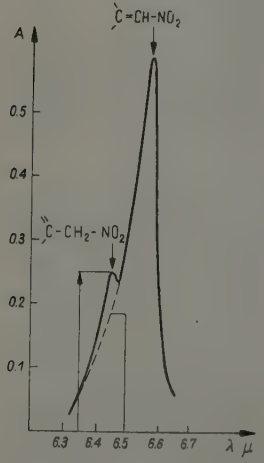


Fig. 4

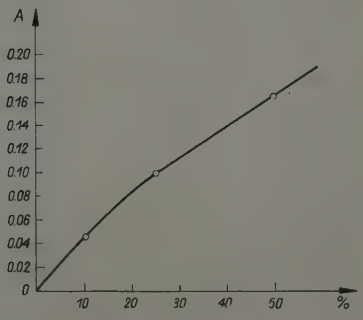


Fig. 5

the straight line tangent to the spectrum curve at the points corresponding to the wave lengths 6.375 and 6.475 μ. The absorption value was determined from the difference $A = A_a - A_b$. The content of the com-

ponent (I) in the mixture of (I) and (II) was determined from the value A by means of the standard curve (Fig. 5).

The values of $\log I/I_0$ were plotted against the concentrations of solutions of the compound (I). The basic 100% concentration was admitted when 2 ml. of the substance were present in 25 ml. of the solution in cyclohexane. The lower concentrations — 50, 25 and 10% — were obtained by the corresponding dilution of the basic solution.

TABLE III

Data for the standard curve

Content of isomer (I) vol %	A_a	A_b	$A=A_a-A_b$	$\overline{A}$
50.0	0.4732	0.2040	0.1692	
	0.4930	0.3320	0.1610	0.1651
25.0	0.2576	0.1540	0.1036	
	0.2602	0.2570	0.1032	0.1034
10.0	0.1126	0.0716	0.0410	
	0.1508	0.0958	0.0550	0.0480

TABLE IV

Analysis of the mixtures of (I) and (II)

Examined sample	A_a	A_b	$A=A_a-A_b$	$\overline{A}$	Content of the isomer (I) vol %
AO_I	0.5087	0.4600	0.0487		
	0.3010	0.2540	0.0470	0.0478	10
AO_{II}	0.2519	0.2100	0.0419		
	0.2669	0.2250	0.0419	0.0419	9
AO_{II} + 50%	0.3936	0.2846	0.1090		
in 50:50 ratio	0.4256	0.3100	0.1156	0.1123	29.5

The values of absorption of these solutions are tabulated (Table III). The values of absorption of two samples of (II), marked AO_I and AO_{II}, are also tabulated below (Table IV). To check the result obtained for the sample AO_{II}, the solution of the sample was mixed with the 50% solution of the isomer (I) in the ratio 50:50. The content of the isomer (I) in the solution thus obtained was next determined by the method described above. The value was in agreement with the expected figure.

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CHEMISTRY

Studies on the Critical Temperature Curves of Mixtures. I. The Azeotropic Range

by

A. KRĘGLEWSKI

Presented by W. ŚWIĘTOSŁAWSKI on December 12, 1956

Introduction

Extensive experimental investigations of two and multicomponent solutions, carried out by Świętosławski and his co-workers, have led recently to a new treatment of the problem of azeotropy. The method consists in studying the boiling temperature isobars formed by an azeotropic agent with the representatives of one or more homologous series. In connection with this, Świętosławski has introduced a characteristic quantity called *azeotropic range* [1], [2]. The azeotropic range $Z_A(H)$ of an agent A with respect to the series of homologues (H) is defined as the difference between the boiling temperatures of the highest and the lowest boiling homologues which form under a given pressure an azeotrope with the agent. Azeotropes formed by these two homologues were called tangent (or almost tangent) azeotropes.

Malesiński [3], [4] has derived from the equations, defining the activity coefficients of the components of a regular solution at the boiling temperatures of the respective binary azeotropes, the following expressions:

$$x_A=\frac{1}{2}+\frac{T_H-T_A}{Z_{AH}}, \qquad x_H=\frac{1}{2}+\frac{T_A-T_H}{Z_{AH}}, \tag{1}$$

$$\delta_A=\frac{1}{2}Z_{AH}x_H^2, \qquad \delta_H=\frac{1}{2}Z_{AH}x_A^2. \tag{2}$$

From (2) results

$$(\sqrt{\delta_A}+\sqrt{\delta_H})^2=\tfrac{1}{2}Z_{AH}, \tag{3}$$

in which δ_i are the azeotropic depressions (T_i-T_{Az}), where T_{Az} is the boiling temperature of the azeotrope, x_i stands for the azeotropic com-

positions in mole fractions, and T_i – the boiling temperatures of the pure components. In deriving them, it was assumed that the vaporisation entropy of agent A is equal to that of components H_i of the series. From this assumption it results that the upper and the lower portions of the azeotropic range are equal to $\frac{1}{2}Z_{AH}$ (symmetrical azeotropic range). Malesiński [5] showed further, on the basis of Świętosławski's scheme of the formation of ternary azeotropes, that for three binary regular solutions (1,2), (2,3) and (1,3) formed by substances 1, 2, and 3, the following relation should be fulfilled:

$$\frac{1}{2}Z_{12}+\frac{1}{2}Z_{23}=\frac{1}{2}Z_{13}, \tag{4}$$

where component 2 has the medium value of the internal pressure.

Critical temperature curves of binary mixtures

Recent experiments on the critical temperature curves of mixtures of non-electrolytes [6]–[8] have shown that there exists some analogy between these curves and the boiling temperature isobars. This is not surprising because both the isobars and the critical temperature curves (in general non-isobaric) may serve as an approximate measure of the deviations from the ideal behaviour. In fact, relations (1), (2) and (3) can be derived from the simplest expression for the critical temperature T^c of a mixture [9]:

$$T^c=T^c x_1^2+2T_{12}^c x_1 x_2+T_2^c x_2^2, \tag{5}$$

x_i being the mole fractions, T_i^c – the critical temperatures of the components (in °K), and T_{12}^c – that of a hypothetical substance, the intermolecular forces of which are acting between unlike molecules of the mixture. In order to derive these relations Equation (5) is transformed as follows:

$$T^c=T_1^c x_1^2+T_2^c x_2^2-(T_1^c+T_2^c-2T_{12}^c)x_1x_2+(T_1^c+T_2^c)x_1x_2, \tag{6}$$

assuming that

$$T_1^c+T_2^c-2T_{12}^c\equiv\frac{1}{2}Z_{12}^c. \tag{7}$$

The azeotropic depressions δ_i in (2) and (3) are then replaced by δ_i^c, which represents the difference between T_i^c and the temperature T_{ex}^c at the extremum point of the critical curve.

The difference between T_{12}^c and the arithmetic mean of T_1^c and T_2^c (identity (7)) is the usually assumed measure of deviation from the ideal solution behaviour. The calculated value of $\frac{1}{2}Z_{AH}$ sometimes changes slightly when computed from δ_A and δ_H for different homologues of the given series. It is therefore reasonable to consider $\frac{1}{2}Z_{AH}$ (and also $\frac{1}{2}Z_{AH}^c$)

as a constant, characteristing a single binary system, the more so that the components may not belong to any homologous series (e. g., carbon dioxide — nitrous oxide system). If the mixture of substances 1 and 2 (or 2 and 3, Eq. (4)) is an ideal solution ($\frac{1}{2} Z_{12} = 0$), then the azeotropic range of agent 3, calculated for both homologues is the same ($\frac{1}{2} Z_{23} = \frac{1}{2} Z_{13}$).

It can be shown that (5) results from a more general expression, when the critical molar volumes of the components are equal to one another and additive [10]. The sulphur hexafluoride — propane system, for which accurate data are available [9], fulfills to some extent these conditions: the critical pressures are 37.10 and 41.93 atm., and the critical densities 5.03 and 4.92 moles/litre respectively; they are, however, not additive. The system forms an azeotrope under the given pressures, and the critical temperature curve possesses a minimum. Table I contains the azeotropic parameters δ_i, δ_j and x_i found graphically from the bubble point data at the three pressures, and $\frac{1}{2} Z$-values calculated by means of (3). Analogous parameters, found for the critical temperature curve, are marked by superscript c. In this case, T_{12}^c is not constant, but varies with composition, and therefore the value at $x = 0.5$ has been substituted into (7). For this reason, the $\frac{1}{2} Z^c$-value calculated according to (7) is less than that found by substituting the values of δ_i^c into relation (3). Both are higher than $\frac{1}{2} Z$ corresponding to the isobars.

Fig. 1 indicates that the liquid densities of the system at several reduced temperatures are not additive [9]. These deviations, particularly in relation to the absolute values of density, increase in the region close to T^c. It will be shown [10] that this is the main cause of the differences between Z and Z^c. It is to be expected that these values should be equal when the volumes are at least approximately additive and if Z changes with the pressure only slightly or not at all. Such properties may be encountered in systems of large non-polar or moderately polar molecules. Some data for such systems are presented in Table II. All the critical temperature curves have been determined by the author. The respective $\frac{1}{2} Z$ values at 1 atm. (i. e., far from the critical region) have been calculated by Malesiński [5]. Small differences between $\frac{1}{2} Z$ and $\frac{1}{2} Z^c$ of the systems formed by benzene, *n*-octane, and the iso-alcohols (except in the benzene — isobutyl alcohol system) can be partly attributed to ex-

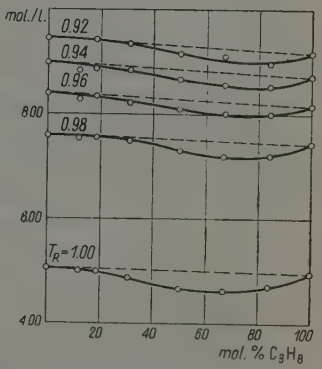

Fig. 1. Bubble point densities of the sulphur hexafluoride — propane system at five reduced temperatures T_R, according to the data of Clegg and Rowlinson [9]

perimental errors. The accuracy of determination of δ^c is about $\pm 0.1°$, i. e., the relative error is large, because the depressions are small. It may be concluded that the azeotropic ranges of these systems are almost constant at all pressures in the whole liquid-vapour coexistence region.

The $\frac{1}{2}Z^c$ value of the pyridine-hydrocarbon systems increases with the molecular weight of the latter. The corresponding value of $\frac{1}{2}Z$ found under atmospheric pressure varies also from 38.0 for the pyridine-heptane, to 42.2 for the pyridine-nonane system [5].

TABLE I

The sulphur hexafluoride (i) — propane (j) system

Pressure atm.	T_i °C	T_j °C	δ_i	δ_j	x_i	$\frac{1}{2}Z$ (Eq. 3)	
22.00	22.35	62.55	0.80	41.00	0.85	53.3	
28.00	32.80	74.70	0.75	42.65	0.85	54.7	
34.00	41.60	85.10	0.65	44.15	0.85	55.5	
	T_i^c	T_j^c	δ_i^c	δ_j^c	x_i	$\frac{1}{2}Z^c$ (Eq. 3)	$\frac{1}{2}Z^c$ (Eq. 7)
critical	45.6	96.7	1.4	52.5	0.83	70.9	64.6

Within the limits of experimental errors, relation (4) is fulfilled for isobars as well as for critical curves. The data for the binary systems formed by pyridine, n-octane and iso-alcohols indicate that, according to (4), $\frac{1}{2}Z^c$ for the pyridine-isobutyl alcohol system is equal to $49.4 - -47.6 = 1.8°$, and that for pyridine and isoamyl alcohol: $49.4 - 41.4 = 8.0°$. The first system is therefore almost ideal, while the second shows positive deviations, a fact confirmed by direct measurements [11].

TABLE II

Components i	Components j	δ_i^c	δ_j^c	$\frac{1}{2}Z^c$ (Eq. 3)	$\frac{1}{2}Z$ (1 atm.) (Eq. 3)
$C_5H_{11}OH$	C_6H_6	18.6	1.1	28.8	—
C_6H_6	C_8H_{18}	1.7	8.5	17.8	18.2
$C_5H_{11}OH$	C_8H_{18}	16.4	5.7	41.4	42.5 *)
C_4H_9OH	C_6H_6	1.5	13.7	24.3	35.0
C_4H_9OH	C_8H_{18}	4.3	23.3	47.6	51.5
C_5H_5N	C_8H_{18}	49.4	0.0 **)	49.4	41.5
C_5H_5N	$C_{10}H_{22}$	13.2	12.5	51.4	—
C_5H_5N	$C_{12}H_{26}$	0.8	41.8	54.2	—

*) data for the heptane-pentanol-2 system.

**) a very flat critical temperature curve, without a minimum, however.

The author wishes to express his thanks to Professor W. Świętosławski for his help and assistance, and to W. Malesiński for many helpful discussions.

Summary

The azeotropic range Z_{ij} of a binary system under low pressures (e.g., 1 atm.) may be calculated in some cases from the critical temperature curve. The role of the volume changes due to mixing is emphasised. The deviations from additivity of the critical temperature curve of a system (i, j) may be calculated from the known curves of systems (i, k) and (j, k) by means of the Malesiński's relation [5],

$$\tfrac{1}{2} Z_{ij} + \tfrac{1}{2} Z_{jk} = \tfrac{1}{2} Z_{ik},$$

derived for regular solutions under isobaric conditions.

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CHEMISTRY

Studies on the Critical Temperature Curves of Mixtures. II. The Binary and Ternary Systems of Acetic Acid-Pyridine-*n*-Paraffins

by

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Presented by W. ŚWIĘTOSŁAWSKI on December 12, 1956

Introduction

The present work is a continuation of previous investigations on the critical temperature curves of non-ideal solutions [1]—[3]. In this paper some selected data are given for binary systems of pyridine with *n*-dodecane, *n*-decane and *n*-octane, and of acetic acid with the same hydrocarbons, including *n*-hexane. The critical temperature surfaces of the ternary systems of pyridine and acetic acid with *n*-dodecane, *n*-decane and *n*-octane have also been determined. Experimental details and all numerical data are being prepared for publication in Roczniki Chemii.

The acetic acid — pyridine system has been previously investigated [1]. The critical temperature curve shows a maximum, at which the critical temperature is 3.5° higher than that of pyridine.

The ternary systems under consideration belong to a class of mixtures, some of which are characterised by the formation of positive-negative (saddle) azeotropes under atmospheric pressure. The peculiar properties of saddle azeotropes have been discussed by Świętosławski [4], [5], and the selected values of azeotropic parameters of the systems of acetic acid and pyridine with *n*-octane and *n*-decane have been summarised by Zięborak [6].

Recently the conclusion has been drawn [7], that there exists a close analogy between the boiling temperature isobars and the critical temperature curves, and that Malesiński's relations determining the azeotropic parameters could be directly applied to these curves. The azeotropic range Z_{AH} of an agent A in relation to the homologous series (H), and the azeotropic depressions δ_A and δ_H are related by the Equation [9]

$$(1) \qquad (\sqrt{\delta_A}+\sqrt{\delta_H})^2=\tfrac{1}{2}Z_{AH},$$

which results from the following two others:

(2a) $\delta_A = \frac{1}{2} Z_{AH} x_H^2$ (2b) $\delta_H = \frac{1}{2} Z_{AH} x_A^2$,

x_A and x_H being the mole fractions of the components in the azeotrope. These relations were derived under the assumption that Z_{AH} remains constant for the whole series of azeotropes (A, H_i). The analogous quantities, found from critical temperature curves, i. e., $\delta_A^c = T_A^c - T_{ex}^c$ and $\delta_H^c = T_H^c - T_{ex}^c$ (T_A^c and T_H^c being the critical temperatures of the components, and T_{ex}^c — that of the extremum point) have been substituted in place of δ_A and δ_H in (1). It was stated [7], that the value, thus calculated, of $\frac{1}{2} Z_{AH}^c$ for systems of non-polar or moderately polar molecules is almost equal to $\frac{1}{2} Z_{AH}$ and corresponding to boiling temperature isobars at atmospheric pressure.

The acetic acid (A) — n-paraffinic hydrocarbon (H) systems

The data presented in Table I (Fig. 1) indicate that the relations (2), predicting a parabolic shape of the line joining the extremum points, are not fulfilled. In fact, the minimum points lie on a nearly straight line. Presumably this may be due to a strong association of acetic acid which is also in its critical region. The real molecular weight is then unequal to the formula weight. The boiling temperature isobars examined under atmospheric pressure are very flat [8]. This might be a sign of the presence of very large clusters of like molecules, existing in systems at temperatures just above their critical liquid—liquid solubility points. On the other hand, the critical temperatures (Fig. 1) decrease abnormally rapidly with the addition of a hydrocarbon to acetic acid. This is probably due to a rapid dissociation of acetic acid dimers by collisions with the neighbouring molecules, owing to their high kinetic energy in the vicinity of the critical region. In spite of the large deviations from the regular solutions behaviour, $\frac{1}{2} Z_{AH}^c$ calculated by means of (1) is almost constant. The mean value of Z_{AH}^c is 268°, i. e., more than twice the Z_{AH} value found by Kurtyka [8] under atmospheric pressure (125°C). The extrapolated broken line in Fig. 1 meets the T-axis about 120° below the critical temperature of acetic acid, in agreement with the calculated va-

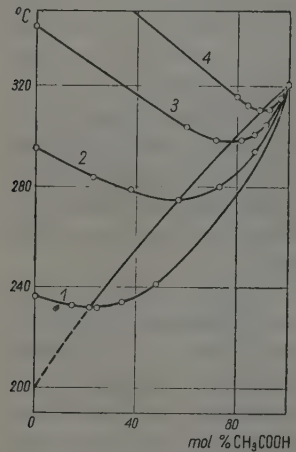

Fig. 1. Critical temperature curves of systems of acetic acid with n-hexane (1), n-octane (2), n-decane (3), and n-dodecane (4)

lue of $\frac{1}{2} Z^c_{AH}$. One can believe that the inequality of Z^c and Z indicates that the azeotropic range increases rapidly with the increase of pressure.

The pyridine (P) — n-paraffinic hydrocarbon (H) systems

The numerical data are given elsewhere [7]. The critical temperature of pyridine T^c_P equals 345°C. The value of $\frac{1}{2} Z^c_{PH}$ calculated from the critical temperature curves with n-octane, n-decane and n-dodecane is about 50°. $\frac{1}{2} Z_{PH}$ under atmospheric pressure equals 40—42° [9].

The ternary acetic acid-pyridine-n-paraffins systems

Several binary mixtures have been mixed with the third component and the critical temperatures of these ternary systems have been determined. From the data thus obtained, together with the data found for binary mixtures, the critical temperature surfaces were constructed for the above mentioned ternary systems.

TABLE I

Critical state of the binary acetic acid-n-paraffinic hydrocarbons systems

Acetic acid ($T^c_A = 321.2°$) with:	T^c_H °C.	T^c_{ex} °C.	δ^c_A	δ^c_H	$\frac{1}{2} Z^c_{AH}$ (Eq. 1)	x_A (± 0.01)
n-hexane	236.7	232.1	89.1	4.6	134	0.220
n-octane	295.6	275.3	45.9	20.3	128	0.565
n-decane	344.3	298.6	22.6	45.7	132	0.775
n-dodecane	386 *)	310.6	10.6	75.4	142	0.900

*) according to International Critical Tables.

Fig. 2 represents the boiling temperature surface at 1 atm. of the acetic acid-pyridine-n-decane system [6]. The negative azeotrope (A,P) shows a large maximum: $\delta_A = -20.0°$, $\delta_P = -22.7°$. The (P,H_{10}) system is zeotropic, because the difference of the boiling temperatures of the components exceeds the value of $\frac{1}{2} Z_{AH}$. The boiling temperature of the saddle azeotrope (S) is 134.4°.

The projections of the critical temperature surface of three ternary systems are commonly drawn in Fig. 3. The top-ridge lines (a), (b), (c) correspond respectively to systems with n-octane, n-decane, and n-dodecane. These lines are shifted much more towards the (P,H) triangle side than those found under atmospheric pressure. This is due to (i) the fact that $Z^c_{AH} \gg Z_{AH}$ (1 atm), and (ii) the decrease of the maximum in the (A,P) system. The probability of the appearance of a saddle point

is therefore less in the critical region. No such point has been found on the critical surface of the systems with *n*-octane and *n*-decane. The acetic acid-pyridine-*n*-dodecane system shows distinctly the existence of a saddle point, characterised by the following values: $T^c = 344.9 \pm 0.1°C.$, composition (in mole per cent): $P - 79$, $A - 12$, $H_{12} - 9$ ($\pm 2\%$). Since the critical pressure of dodecane is much lower than that of either pyridine or acetic acid, the saddle azeotrope, if it exists in the critical region, will have a composition differing from that at the saddle point on the critical temperature surface. On the other hand, in systems the components of which have equal or almost equal critical pressures (and temperatures), the eventually existing azeotrope may have in the critical region a composition close to that at the extremum point of the critical curve. Such is believed to be the case in the acetic acid – pyridine system [1].

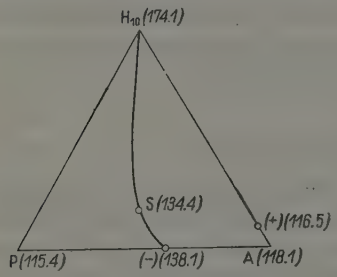

Fig. 2. Boiling temperature surface (at 1 atm.) of the pyridine (P) – acetic acid (A) – *n*-decane (H_{10}) system, according to Turski [6]. ⊙ – azeotropic points ((+) – positive, (–) – negative, S – saddle point).

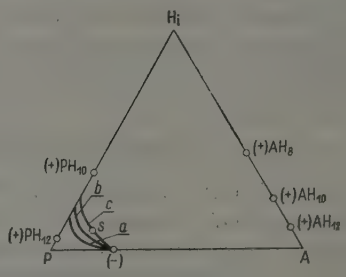

Fig. 3. Critical temperature surface of the systems formed by pyridine (P) and acetic acid (A) with *n*-octane (H_8), *n*-decane (H_{10}), and *n*-dodecane (H_{12}) ⊙ – extremum points ((+) – minimum, (–) – maximum, S – saddle point)
Top-ridge lines corresponding to systems: (*a*) – A, P, H_8, (b) – A, P, H_{10}, (c) – A, P, H_{12}.

The author is greatly indebted to Professor W. Świętosławski for suggesting these investigations.

Summary

Selected data are given for the critical temperature curves of binary systems formed by acetic acid (A) and pyridine (P) with *n*-hexane, *n*-octane, *n*-decane and *n*-dodecane. The critical temperature surfaces have been determined for the ternary A, P systems with *n*-octane, *n*-decane and *n*-dodecane. The surface of the latter shows a saddle point.

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CHEMISTRY

Vibration Spectra and Force Constants of Nitriles

by

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Presented by W. KEMULA on December 20, 1956

The aim of this paper was to investigate the dependence of the vibration spectra of molecules containing the $C-C\equiv N$ and $C=C-C\equiv N$ bond systems on their structures.

We calculated the approximate values of the force constants and frequencies of vibration of three groups of molecules: (a) saturated nitriles: acetonitrile (I) and malonitrile (II); (b) unsaturated nitriles: acrylonitrile (III), methylacrylonitrile (IV), nitriles of crotonic (trans) acid (V), isocrotonic (cis) acid (VI) and (c) cyanogen (VII). For all the molecules of each of these groups we used the same assembly of force constants and obtained satisfactory agreement between the calculated and the observed frequencies.

This type of systematic calculation for the entire group of nitriles has been made for the first time in the present investigation. So far, only the calculations of the vibrations of some individual molecules based on the more simplified models [1], [8] were known. In performing our calculations, we used the experimental values of the vibration frequencies from papers published previously [2], [5], [9]—[12]. For the above-mentioned molecules there is a lack of data, except for acetonitrile and cyanogen [16], concerning the length of the bonds and the size of the angles. For this reason we assumed that the lengths of the corresponding bonds in each of the groups mentioned above *) were equal. For the tetrahedral and trigonal angles we used the theoretical values (Fig. 1). The fact that the vibrations were anharmonic was taken into account by assuming the "spectroscopic mass" of hydrogen [19].

We made the calculations by the method of Elyashevich and Stepanov [13]. The co-ordinates of the CH_3 and CH_2 groups of atoms were

*) The most probable values for the length of the bonds were chosen by comparison with the molecules containing analogous bond systems whose geometrical parameters are known.

eliminated on the basis of their approximate symmetry. We did not perform calculations for non-planar vibrations. The secular equation was solved by the method of successive eliminations, since the use of more accurate methods, in face of the approximations applied, would have served no purpose.

Table I lists the force constants of the individual groups of molecules. The force constants are given everywhere in units of 10^6 cm.$^{-2}$ (1 cm.$^{-2}$ = 0.06365 dyne/cm.). We adopted the following notations for the force constants: K — diagonal constant, H — interaction between the bonds; A — interaction of the bond with the adjacent angle; l — interaction of two adjacent angles; m and n — interactions between angles with a common bond; the indices refer to the interacting co-ordinates (for the notations as regards the co-ordinates, see Figs. 1, 2, 3). The constants with an asterisk were taken from [13] and [14] in connection with the spectrum of ethane and ethylene; the remaining force constants were determined by the variation method.

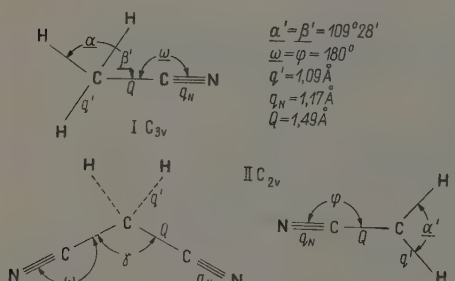

Fig. 1

The calculated frequencies of vibration are collected in Table II, together with the most convincing experimental values. Since only the Raman spectra are known for the molecules IV, V and VI, we tried, during the calculations, to obtain everywhere agreement of the spectra in the liquid phase. The mean deviation is 12 cm.$^{-1}$ and the maximum deviation 42 cm.$^{-1}$. The results of the calculations show that, in the first approximation, the force constants of the molecules of each group are the same. Some calculated frequencies have no corresponding values in the Raman spectra (IV, V). Since all frequencies of these molecules theoretically possible in the Raman spectra have not been found, and since, in general, very weak Raman lines correspond to given normal vibrations, we believe that the cause of the disagreement lies in the lack of complete experimental data.

Comparison of the force constants and the frequencies of vibration permits certain conclusions to be drawn as regards the structure of the molecules considered.

The force constant of the single C—C bond in aliphatic hydrocarbons is $K_Q = 7.02$. In the aliphatic nitriles, its value already increases to 8.0, probably as a result of the hyperconjugation of the C≡N bond with the CH_3 or CH_2 groups. Because of the conjugation of the bonds in ethylene nitriles, there appears a further strengthening of the C—C

bond ($K_Q = 8.3$), and finally, in cyanogen, the force constant ($K_Q = 10.0$) does not greatly differ from the force constant of the C—C bond in benzene ($K_Q = 11.35$) [15]. At the same time, the force constant of the C≡N bond is reduced from $K_N = 28.0$ in I and II to $K_N = 27.5$ in III, IV, V, VI, and finally to $K_N = 27.3$ in VII. The force constant of the C=C bond, however, achieves the same value in molecules III—VI as in ethylene. The results of these calculations are in agreement with the measurements of the inter-atomic distances: the lengths of the C—C bond in aliphatic hydrocarbons are 1.54 Å, 1.49 Å in I and 1.37 Å in VII, while the lengths of the multiple bonds do not undergo any visible change.

The interpretation of the low frequencies and, above all, the strong lines of frequency of about 150—250 cm.$^{-1}$, characteristic for nitriles, has caused much difficulty till now. They have been generally ascribed to the non-planar deformation vibration of the —C≡N group [16]. Only Halverson [2], [5] interpretes them, in the case of molecules II and III, as plane, symmetrical vibrations.

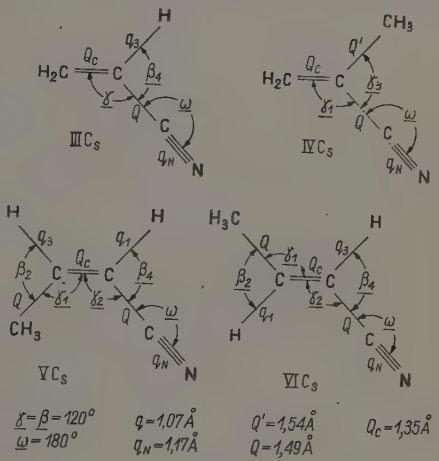

Fig. 2

It results from our calculations that within the ranges of 150—240 and 500—750 cm.$^{-1}$ there appear, as a result of mechanical resonance and strong "repulsion", the frequencies of plane vibrations of the γ and ω co-ordinates. On the other hand, the frequencies of about 350 cm.$^{-1}$ (near the frequency of vibration of the ω-angle in I) are, in general, characteristic for ω non-planar vibrations, where there are no strong interactions with other co-ordinates. The strong interaction of the ω-angles vibrations appears also in VII and leads to the appearance of the frequencies 226 and 506 cm.$^{-1}$.

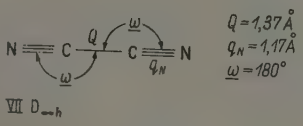

Fig. 3

We have established that the alkyl groups have only an insignificant influence on frequencies we are concerned with (they have a larger influence on the frequencies corresponding to the normal vibration of the β-angles). Consequently, we believe that the results of our calculations can be used for interpreting the spectra of more complex molecules containing the C—C≡N and C=C—C≡N bond systems.

We express our gratitude to Professor W. Kemula for his constant interest in the work and to Professor P. A. Bazhulin for valuable discussion and critical remarks.

TABLE I

Force Constants

Co-ordinate	Saturated Nitrile	Unsaturated Nitrile	Cyanogen
$K_{q'}$	8.08 *)	8.08 *)	—
K_q	—	8.63 *)	—
K_Q	8.0	8.3	10.0
$K_{Q'}$	—	7.02 *)	—
K_C	—	14.2 *)	—
K_N	28.0	27.5	27.3
$K_{\alpha'}$ (—CH_3)	0.71 *)	0.71x	—
$K_{\alpha'}$ ($\rangle CH_2$)	0.65	—	—
K_α	—	0.55 *)	—
$K_{\beta'}$ (—CH_3, $\rangle CH_2$)	0.92	0.92 *)	—
K_β (=CH_2)	—	0.77 *)	—
K_β (CH.CN)	—	0.65	—
K_β (CH.CH_3)	—	0.70	—
K_γ	0.8	1.1	—
K_ω	0.45	0.45	0.425
$H_{q'q'}$	0.05 *)	0.05 *)	—
H_{qq}	—	0.03	—
H_{Qq}	0x	0x	—
H_{Cq}	—	0.1	—
H_{QC}	—	0.1	—
H_{QQ}	0.05 *)	0.05 *)	—
H_{QN}	0.5	0.5	0.5
$A_{q'\alpha'}$	0.35 *)	0.35 *)	—
$A_{q'\beta'}$	0.35 *)	0.35 *)	—
$A_{q\alpha}$	—	0.43 *)	—
$A_{q\beta}$	—	0.66 *)	—
$A_{Q\beta(p')}$	0.43 *)	0.43 *)	—
$A_{C\beta}$	—	0.45 *)	—
$A_{Q\gamma}$	0.3	0.7	—
$A_{C\gamma}$	—	0.8	—
$A_{Q\omega}$	0.3	0.3	—
$A_{N\omega}$	0.5	0.5	—
l	−0.035 *)	−0.035 *)	—
n	0.12	0.1	—
m	−0.025	−0.02	−0.02

(for angles lying in different planes $m, n = 0$).

*) force constants from [13] and [14].

TABLE II

Vibration Frequency

Species and Co-ordinate	Calculated	Observed R [10]	Observed IR [9] (gas)	Observed IR (liquid)
	Acetonitrile $CH_3.CN$			
A				
(Q)	911	918	920	
(β')	1380	1376	1400	
(q_N)	2240	2249	2267	
(q)	2900	2942	2965	
E				
(ω)	381	380	361	
(β')	1059	—	1041	
(α')	1461	1445	1454	
(q)	2998	2997	3009	
	Malonitrile $CH_2.(CN)_2$			
		[11]	[2]	[2]
A_1				
(γ, ω)	141	167	—	—
(γ, ω)	579	574	582	582
(Q)	880	892	892	893
(α')	1405	1386	1422	1395
(q_N)	2258	2263	2274	2275
(q)	2928	2929	2951	2935
B_1				
(ω)	367	367	—	—
(Q)	980	975	982	984
(β')	1306	1310	1322	1320
(q_N)	2267	2263	2274	2275
A_2				
(φ)	374	367?	—	—
(β')	1245	1214	1225	1218
B_2				
(φ)	381	367?	—	—
(β')	911	—	—	936
(q)	2976	2968	2976	2968
	Acrylonitrile CH_2:CH.CN			
		[5]	[5]	[5]
A'				
(γ, ω)	283	242	—	—
(γ, ω)	561	570	—	—
(Q)	877	871	871	871
(β)	1282	1286	1282	1288
(Q_C)	1611	1607	1615	1609
(q_N)	2220	2228	2239	2228
(q_3)	3053	3068	—	3068

Vibration Frequency

Species and Co-ordinate	Methyl-acrylonitrile $CH_2{:}C(CH_3).CN$			
	Calculated	Observed R [10]	Observed IR [9] (gas)	Observed IR (liquid)
		[12]		
A'				
(γ,γ,ω)	160	201		
(γ,γ,ω)	500	—		
(γ,γ,ω)	548	530		
(Q)	753	749		
(Q')	1122	—		
(Q_C)	1609	1625		
(q_N)	2226	2224		

Species and Co-ordinate	Nitrile of Crotonic Acid (trans) $CH(CH_3){:}CH.CN$		Nitrile of Isocrotonic Acid $CH(CH_3)+CH.CN$	
	Calculated	Observed R [12]	Calculated	Observed R [12]
A'				
(γ,γ,ω)	200	182	150	170
(γ,γ,ω)	410	395	370	393
(γ,γ,ω)	670	—	650	—
(Q)	903	891	897	888
(Q')	1093	1103	1093	1100
(β_4)	1233	1228	1243	1225
(β_3)	1345	1310	1342	1365
(Q_C)	1648	1632	1643	1626
(q_N)	2230	2220	2228	2217
(q_3)	3044	3028	3045	3050
(c_1)	3060	3079	3057	3075

Cyanogen $(CN)_2$

Species and Co-ordinate	Calculated	Observed [17], [18]		
$\sigma_g^+(Q)$	843	848 R		
(q_N)	2351	2322 R		
$\sigma_u^+(q_N)$	2149	2149 IR		
$\pi_g\ (\omega)$	506	506 R		
$\pi_u\ (\omega)$	226	226 IR		

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CHEMISTRY

Influence of Medium Acidity on the Structure of Nitric Acid

by

S. MINC, Z. KĘCKI and S. OSIECKI

Presented by M. ŚMIAŁOWSKI on January 18, 1957

In the investigation of Raman spectra of $HNO_3-CH_3COOH-H_2O$ solutions reported in a previous work [1] it was found that the intensity of the 1300 cm.$^{-1}$ line (corresponding to the symmetric valence vibrations of the $HONO_2$ molecule) increases more rapidly than the concentration of undissociated nitric acid. Taking into account the nature of the 1300 cm.$^{-1}$ vibration and the structure of the HNO_3 molecule we came to the conclusion that the increase of the Raman quantum efficiency is due to an increase of the polarity of the $HO-NO_2$ bond. We have found that the acidity of the solution has an influence on this phenomenon, i. e., high acidity not only causes dissociation of nitric acid to diminish, but also changes the polarity of bonds in the undissociated $HONO_2$ molecule.

At the same time we predicted that this fact would, among others, have a consequence in the course of cathodic polarization [3], [4], namely — that the greater the acidity of the HNO_3 solutions, the greater would be the domination of the high potential range.

The aim of the present work was an experimental confirmation of our views and conlcusions drawn from the above facts. The Raman spectra which we investigated were made on $HNO_3-H_2SO_4-H_2O$, $HNO_3-HClO_4-H_2O$ and — in order to make a comparison — on $HNO_3-CH_3COOH-H_2O$. For several solutions of $HNO_3-H_2SO_4-H_2O$ and $HNO_3-CH_3COOH-H_2O$ systems we also determined the cathodic polarization curves.

Experimental work

The following ternary solutions were made: $HNO_3-H_2SO_4-H_2O$, $HNO_3-HClO_4-H_2O$ and $HNO_3-CH_3COOH-H_2O$. The total concentrations

of both acids were determined in each case by titration; the concentration of HNO_3 — by Lunge's nitrometric method.

Spectra of the solutions were obtained by an ISP-51 type spectrograph with a camera having a focus of 120 mm., using a slit width of 0.020 mm. (corresponding to 3 cm.$^{-1}$), the time of exposition being 20 minutes. The exciting light source was a PRK-2 type mercury lamp operating at a stabilised current of 3.7 ± 0.05 A. inside a Zeiss-type reflector. The exciting light passed through a filter containing an almost saturated solution of sodium nitrite.

The spectra were recorded on ortochromatic antihalo plates having a contrast coefficient of 2.2, produced by Bydgoskie Zakłady Fotochemiczne. On each plate 3 expositions of a 9-grade optical neutral wedge were made so as to obtain the characteristic curve of the emulsion.

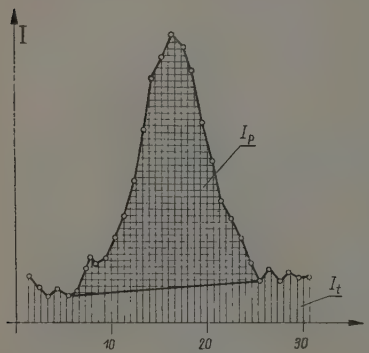


Fig. 1

Measurements of blackening were made by means of an MF-2 type spectrum-line photometer without recorder. The blackenings of the *e*-1050 cm.$^{-1}$ and 1300 cm.$^{-1}$ lines corresponding to the NO_3^- ion and the $HONO_2$ molecule respectively were measured on a number of points in the neighbourhood of maxima of these lines. Basing on the characteristic curve of the emulsion the blackenings were converted into intensities and the contour of the line under investigation was drawn (Fig. 1). The area under the contour had been determined by cutting out and weighing on an analytical balance *).

Determination of the integral intensities was necessary in this case because an overlapping takes place **) of the 1050 cm.$^{-1}$ line of the NO_3^- ion and the 1047 cm.$^{-1}$ line of the HSO_4^- ion. To eliminate the participation of the 1047 line in the intensity of the NO_3^- line the integral intensities of the HSO_4^- ion line in aqueous solutions of H_2SO_4 were measured and the dependence of the *e*-1047 intensity on the H_2SO_4 concentration was plotted. From the intensities of the investigated NO_3^- ion line the values taken from the plot mentioned above were subtracted and the difference obtained was considered to be the intensity of the sole NO_3^- ion.

*) A check was made to establish the constancy of weight per unit area of the paper used. Maximum deviations from the mean were at most 5 per cent.

**) The spectra of the HNO_3—$HClO_4$—H_2O and HNO_3—CH_3COOH—H_2O systems do not show such overlapping.

It was feared that the light absorption due to evolving nitric oxides in the solution and differences of the refractive index of different solutions might have an extra effect on the intensities determined. The influence of these factors was eliminated by a method described in one of our previous papers [2]. For wave lengths of 436 mμ (Hg *e*), 457 mμ (*e*-1050) and 462 mμ (*e*-1300), absorption measurements were performed by means of a "Unicam" spectrophotometer. Measurable absorption was found only in 3 solutions of the HNO_3–H_2SO_4–H_2O system. The other did not show this behaviour in the wave length ranges under review. The refractive index was measured on a Pulfrich refractometer at room temperature for the *D*-line of sodium.

Analogously to a previous work [1], the quantum efficiency of the *e*-1050 line was taken as constant; hence, it was possible – basing on the intensities of this line – to determine the concentration of the dissociated form of HNO_3.

The standard was an aqueous solution of sodium nitrate having a concentration of 0.95 mole/l.

The concentration of the undissociated part of HNO_3 was calculated as the difference between the stoichiometric concentration of the acid and the concentration of the dissociated form.

The relative quantum efficiencies of the *e*-1300 line in the investigated solutions were computed taking one of them (HNO_3 5.98 mole/l., H_2SO_4 5.10 mole/l., the rest being H_2O) as the reference solution, the quantum efficiency of the *e*-1300 of this solution being taken arbitrarily as unity.

The results obtained are given in Table I.

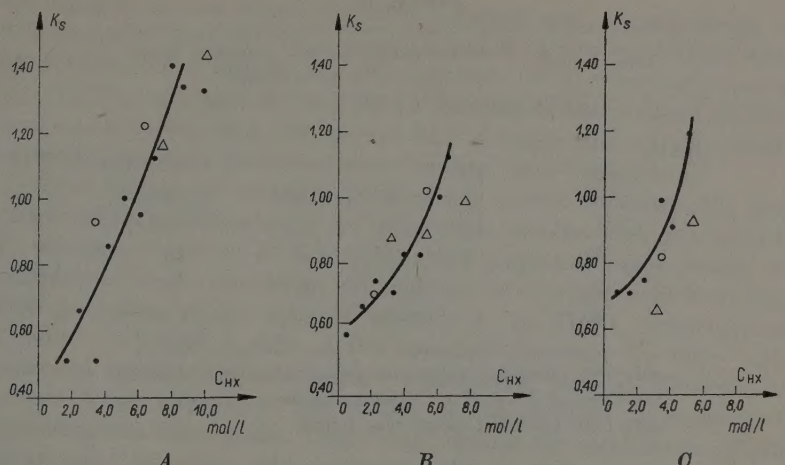
Fig. 2 represents a plot of the quantum efficiency of the *e*-1300 line ($HONO_2$) against the acidity of the medium at constant HNO_3 concentration.

Moreover, the cathodic polarization curves in solutions of the HNO_3–CH_3COOH–H_2O and HNO_3–H_2SO_4–H_2O systems were determined. Fig. 3 contains some exemplifying curves. In the Tables II and III the polarizing current densities are given, at which the transition from the high- to low-potential range occurs.

In order to accomplish the investigations of Raman spectra of the solutions considered it was necessary to make certain assumptions which may influence the computed values. The first of these assumptions was the constancy of the quantum efficiency of the *e*-1050 line of the NO_3^- ion. The fear however exists that in strongly acid solutions the NO_3^- ion undergoes distortion and this would cause the quantum efficiency of the *e*-1050 line to diminish with increasing acidity. In such a case the values of quantum efficiency computed for the *e*-1300 line would be too low in comparison with the real ones.

TABLE I

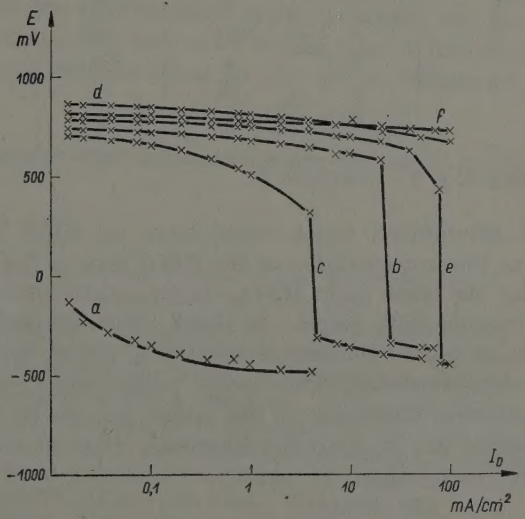
	Concentration mole/l.							Relative quantum efficiency of e-1300 cm.$^{-1}$ line
	HNO_3	H_2SO_4	$HClO_4$	CH_3COOH	NO_3^-	$HONO_2$	% $HONO_2$	
1	3.88	—	5.19	—	0.97	2.91	75.0	0.97
2	3.71	—	8.10	—	—	3.71	100	1.43
3	3.94	—	—	12.70	0.93	3.01	76.4	1.64
4	6.42	1.55	—	—	3.35	3.07	47.8	0.51
5	6.23	2.37	—	—	3.13	3.10	49.8	0.66
6	5.84	—	3.35	—	1.95	3.89	66.6	0.93
7	6.00	3.36	—	—	2.20	3.80	63.3	0.51
8	5.98	4.15	—	—	2.12	3.86	64.5	0.86
9	5.98	5.10	—	—	1.10	4.88	81.6	1.00
10	5.98	5.98	—	—	0.87	5.11	85.5	0.95
11	5.64	—	6.27	—	—	5.64	100	1.22
12	5.90	6.88	—	—	0.68	5.22	88.8	1.12
13	5.92	—	—	7.35	2.73	3.19	53.9	1.16
14	5.70	8.00	—	—	0.53	5.17	90.7	1.40
15	5.61	8.73	—	—	0.49	5.12	91.3	1.34
16	5.37	9.86	—	—	0.52	4.85	90.3	1.33
17	5.88	—	—	10.00	1.23	4.65	79.1	1.43
18	8.06	0.50	—	—	4.01	4.05	50.2	0.58
19	8.15	1.47	—	—	3.32	4.83	59.3	0.67
20	8.01	—	2.22	—	2.65	5.46	68.2	0.70
21	7.64	2.28	—	—	2.95	4.69	61.4	0.75
22	8.01	—	—	3.21	3.92	4.09	51.1	0.88
23	8.11	3.35	—	—	1.84	6.27	77.3	0.71
24	8.25	4.02	—	—	1.26	6.99	84.7	0.83
25	8.15	4.98	—	—	0.75	7.40	90.8	0.83
26	8.08	—	—	5.23	2.69	5.39	66.7	0.89
27	7.64	—	5.34	—	—	7.64	100	1.02
28	7.86	6.07	—	—	0.63	7.23	92.0	1.00
29	8.12	6.53	—	—	0.74	7.38	90.9	1.12
30	8.13	—	—	7.60	1.73	6.40	78.7	0.99
31	9.90	0.92	—	—	3.56	5.34	53.9	0.71
32	10.02	1.43	—	—	2.95	7.77	77.5	0.71
33	10.10	2.29	—	—	1.91	8.19	81.1	0.75
34	10.07	—	—	3.05	2.82	7.25	72.0	0.66
35	9.54	—	3.30	—	1.27	8.27	86.7	0.82
36	9.84	3.37	—	—	1.49	8.35	84.9	0.99
37	9.78	4.00	—	—	0.91	8.87	90.7	0.91
38	9.76	5.03	—	—	0.73	9.03	92.5	1.19
39	9.75	—	—	5.20	1.80	7.95	81.0	0.93



$HX = H_2SO_4$; $HClO_4$; CH_3COOH; • = HNO_3—H_2SO_4—H_2O; ○ = HNO_3—$HClO_4$—H_2O; △ = HNO_3—CH_3COOH—H_2O

A.—$C_{HNO_3} \simeq 6$ mole/1 *B*.—$C_{HNO_3} \simeq 8$ mole/1 *C*.—$C_{HNO_3} \simeq 10$ mole/1.

Fig. 2. Dependence of relative quantum efficiency of the *e*-1300 cm.$^{-1}$ line on concentration of acids



a — 1 m. HNO_3; *b* — 4 m. HNO_3; *c* — 1 m. HNO_3 — 10 m. CH_3COOH; *d* — 1 m. HNO_3 — 15 m. CH_3COOH; *e* — 1 m. HNO_3 — 5. H_2SO_4; *f* — 4 m. HNO_3^- 3,5 m. H_2SO_4.

Fig. 3. Cathodic polarization curves of the solutions

TABLE II

Conc. mole/l. HNO_3 \ CH_3COOH	Transition to low potential range at mA/cm.² 0	5	10
0	—	0.04	0.04
1	*a*	*a*	4.5
2	4	4	20
3	5	50	*b*
4	25	*b*	*b*

a — only low potential range of polarization was found in the interval covered by measurements
b — only high potential range was found.

TABLE III

Conc. mole/l. HNO_3 \ H_2SO_4	Transition to lower potential range at mA/cm.² 0	2	3.5	5
0	—	*a*	*a*	*a*
1	*a*	2.5	50	90
2	4	6	175	*b*
3	5	25	*b*	*b*
4	25	80	*b*	*b*

For the meaning of *a*, *b* — see Table II.

The second assumption which could have an effect on the computed results, was the concentration of the HSO_4^- ions in the H_2SO_4—H_2O solutions as being the same as in HNO_3—H_2SO_4—H_2O solutions of equal analytic concentrations with respect to H_2SO_4. This played a role when the participation of the *e*-1047 line of the HSO_4^- ion in the intensity of the *e*-1050 line was regarded. This factor might cause the computed values of the quantum efficiency of the *e*-1300 line to be too high.

As both factors act in opposite directions, they should — at least partially — cancel each other.

Conclusions

An increase in the acidity of the medium not only caused the dissociation of nitric acid to diminish, but also the Raman quantum efficiency of the *e*-1300 line to rise. This line corresponds to vibrations of the undissociated HNO_3 molecule. The elevation of its efficiency indicates

the polarity of the bonds between nitrogen and oxygen atoms of the NO_2-group to decrease. In a previous paper [1] we established that this phenomenon was caused by the influence of the medium exerted on the $HONO_2$ molecule. It leads to an increase of the polarity of the bond between the NO_2 and OH groups and a weakening of this bond. The experimental data presented here confirm such conclusions.

The course of cathodic polarization curves indicates the undissociated $HONO_2$ molecules to be responsible for the high potential range. In aqueous solutions of HNO_3 the high potential range starts at concentrations of 3—4 moles/l.; on addition of another acid however, this high potential range appears already at an HNO_3 concentration of 1 mole/l., whereby a shift of the boundary between the high- and low-potential ranges, towards greater polarization current densities, is observed, if an increase of the acidity of the medium at constant HNO_3 concentration takes place. These data confirm the mechanism of cathodic polarization in nitric acid solutions given by Minc [3], [4].

In the papers of several investigators [5]—[10] the opinion predominates that the nitronium ion NO_2^+ is the nitrating agent for aromatic compounds. There is no unique opinion however [5], [10], [11] as to how to explain the behaviour of such nitrating mixtures as HNO_3-water solutions of moderate concentrations or the mixture HNO_3—CH_3COOH—H_2O, since in these systems the presence of nitronium ions has not been found. In our opinion the undissociated HNO_3 molecules are the nitrating agent in these solutions. The molecules should have a polarized and weakened HO—NO_2 bond corresponding to the given compound undergoing nitration.

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